Carbohydrate Research 375 (2013) 118–135

Contents lists available at SciVerse ScienceDirect

Carbohydrate Research

journal homepage: www.elsevier.com/locate/carres

Synthesis of a chlorogenin glycoside library using an orthogonal protecting group strategy

Ying-Hsin Wang [a,†], Hsien-Wei Yeh [a,†], Hsiao-Wen Wang [a], Chia-Chun Yu [a], Jih-Hwa Guh [a], Der-Zen Liu [b], Pi-Hui Liang [a,*]

[a] School of Pharmacy, College of Medicine, National Taiwan University, 1 Jen-Ai Road, Section 1, Taipei 100, Taiwan
[b] Graduate Institute of Biomedical Materials and Tissue Engineering, College of Oral Medicine, Taipei Medical University, Taipei, Taiwan

ARTICLE INFO

Article history:
Received 21 February 2013
Received in revised form 12 April 2013
Accepted 13 April 2013
Available online 28 April 2013

Keywords:
Chacotriose
Glycoside
Cytotoxicity
Dioscin

ABSTRACT

Naturally occurring spirostanol saponins bear a chacotriose, α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→4)]-β-D-glucopyranose residue as the oligosaccharide moiety which is believed to be important for biological activity. Herein the development of a concise, combinatorial method for the synthesis of two series of glycan variants at the 2′ and/or 4′ positions of chacotriose is described and the structure–activity relationships of the glycone part at 3-OH of chlorogenin investigated. These compounds were found to be weakly-cytotoxic toward leukemia cell lines CCRF and HL-20, indicating that the chacotriose moiety is important for anticancer activity.

1. Introduction

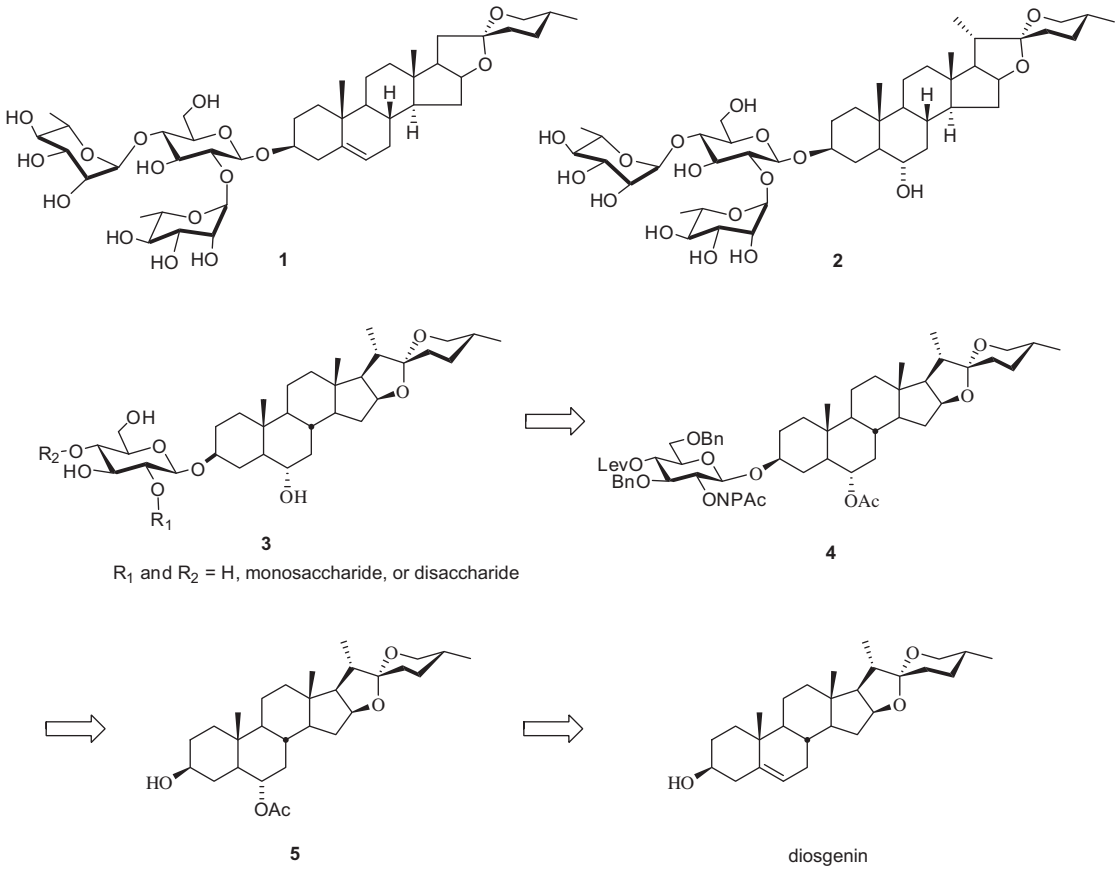
Steroidal saponins are steroidal glycosides and can be divided into two major groups, spirostanosides and furostanosides. Spirostanosides bear one sugar chain, generally at the C-3 position, and furostanosides bear two sugar chains, one at the C-3 and the other at the C-26 positions.[1] Dioscin (**1**, Scheme 1), which bears a chacotriosyl (α-L-rhamnopyranosyl-(1→2)-[α-L-rhamnopyranosyl-(1→4)]-β-D-glucopyranosyl) moiety at the 3-OH of diosgenin, is one of the most commonly occurring spirostanosides, occurring widely in plants. Amongst the wide range of bioactivities that spirostannosides exhibit, hemolytic and cytotoxic activities are the two most commonly observed activities, and recent studies have shown that dioscin can induce apoptosis within tumor cells.[2–4] A few structure–activity relationship (SAR) studies of dioscin have been documented[5–7] indicating that subtle modification of the glycan portion is well tolerated. Recently, chlorogenin 3-*O*-β-chacotrioside (**2**) and its derivatives were reported to be potent entry inhibitors of the H5N1 influenza virus.[8,9] The SAR study indicated that the sugar part is important for bioactivity.

Many of these bioactive compounds contain sugar units, which are often required for function in vivo. Glycosylation of natural products may affect solubility, stability, or molecular recognition associated with the biological target.[10,11] Modification of the carbohydrate domain of natural products may lead to a better understanding of the recognition process and has potential to identify new therapeutics. Consequently, the development of practical methods to create a library of glycosides might help to achieve these goals. To date, two general strategies for the construction of saponins have been disclosed: a convergent approach (Route 1, Scheme 2), in which the aglycon is directly glycosylated with a prefabricated sugar donor;[12–15] and a linear synthesis (Route 2, Scheme 2), in which the aglycon is glycosylated with a monosaccharide, and subsequently elongated via a series of protecting group manipulations.[16–23] Both strategies have been applied to the synthesis of dioscin derivatives,[12–23] but each has limitations. The first is efficient, but is limited to a specific fabricated sugar donor, and glycosylation with an oligosaccharide donor which contains a (1→2)-linkage at the reducing end where no neighboring-group participation can be exploited, the glycosylation would be low yielding due to the low selectivity of 1,2-tans-glycosylation. In fact, such type of oligosaccharides is common in natural saponins.[24] The second is inefficient, due to the laborious protecting group manipulations required between each glycosylation step. Orthogonal protecting group strategies[25,26] have been developed to alleviate these problems, at least in part.

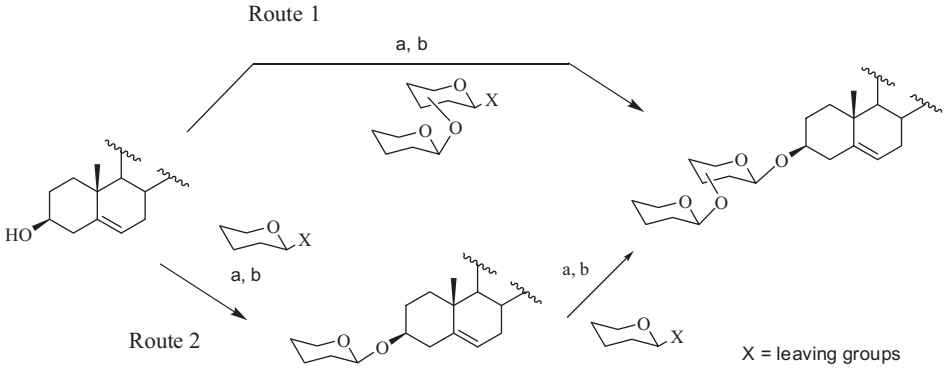
Most of the aforementioned SAR studies maintained a rhamnose moiety at the 2′- and 4′-positions of the chacotriose moiety (e.g., **1** & **2**, Scheme 1) and SAR studies of analogs bearing alternative saccharides at these positions are yet to be conducted. We have developed a concise and combinatorial strategy to construct the saccharide library **3** of chlorogenin. Compound **4** was identified

* Corresponding author. Fax: +886 2322 5095.
E-mail address: phliang@ntu.edu.tw (P.-H. Liang).
† These authors contributed equally to this work.

0008-6215/$ - see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.carres.2013.04.022



Scheme 1. Structure of **1** and **2** and a possible approach for modification of chlorogenin to give a library of **3** which can be retrosynthesized from diosgenin.



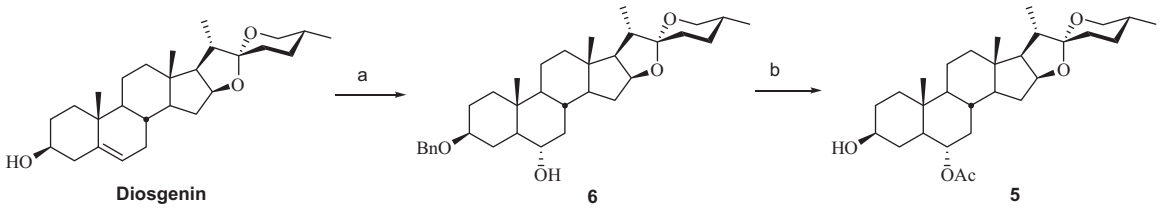
Scheme 2. Two synthetic strategies toward saponins. Route 1 is a convergent approach. Route 2 is the linear approach. (a) Glycosylation step; (b) Protective group manupulations.

as the key intermediate (Scheme 1), in which 2-nitrophenylacetyl[27] and levulinoyl groups were chosen to protect the 2- and 4-positions of glucose, respectively. Orthogonal deprotection of core **4** followed by combinatorial glycosyltion with various glycoyl donors, yielded a library of chlorogenin (**3**) analogs.

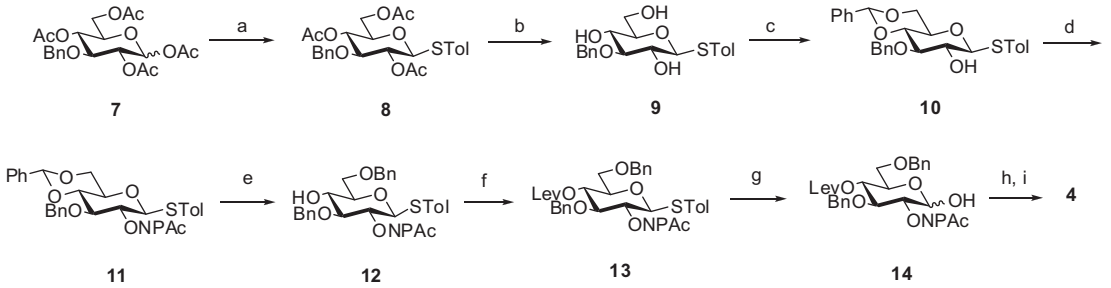
2. Results and discussion

The synthetic route to glycosyl acceptor **5** is depicted in Scheme 3. After the 3-OH of diosgenin was protected with a benzyl group, hydroboration–oxidation of the 5,6-double bond introduced 6α-OH, to give compound **6**.[21] The newly formed alcohol at 6-position was acetylated, and the 3-OBn was removed by Pd/C-catalyzed hydrogenolysis to give glycosyl acceptor **5** for later use.

To synthesize the core structure **4**, compound **7**,[28] was prepared from 1,2,5,6-diisopropylidene-D-glucose (Scheme 4), treatment with *p*-thiotoluene and $BF_3{\cdot}OEt_2$ in CH_2Cl_2 to give thioglycoside **8**. Compound **8** was subjected to ester hydrolysis by cat. NaOMe in MeOH to give **9**, and then the 4,6-diol group was protected to give the benzylidene acetal **10** by treatment with benzaldehyde dimethyl acetal in acetonitrile (ACN), in the presence of camphorsulfonic acid (CSA). 2-Nitrophenylacetyl (NPAc) group was chosen for installation at 2-OH of compound **10**, as it could selectively be removed through zinc-catalyzed reduction[27] when desired and can also help in imparting β-selectivity during the glycosylation through neighboring group participation. The 2-OH of **10** was thus protected with NPAc, installed by treating with NPAcOH in the presence of dicyclohexylcarbodiimide (DCC)



Scheme 3. Reagents and conditions: (a) (i) NaH, BnCl/THF, DMF, 0–60 °C, 15 h; (ii) BH_3/THF, 0 °C to rt, 12 h; (iii) 10 N NaOH, H_2O_2, rt, 2 h, 32% three steps; (b) (i) Ac_2O/pyridine, DMAP, 0 °C to rt; (ii) H_2, Pd/C, rt, 12 h, 92% two steps.

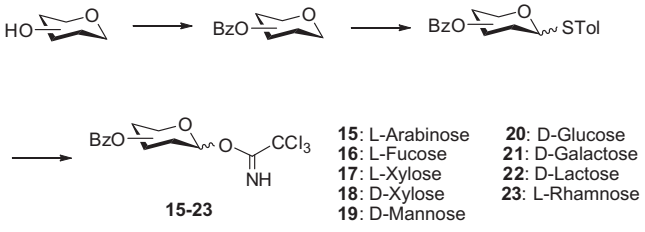


Scheme 4. Reagents and conditions: (a) *p*-toluenethiol, $BF_3{\cdot}OEt_2/CH_2Cl_2$, 0 °C to rt, 8 h, 73%; (b) NaOMe/MeOH, rt, 12 h, 87%; (c) benzaldehyde dimethyl acetal, CSA/ACN, rt, 4 h, 76%; (d) (2-nitro)phenylacetic acid, DCC, DMAP/CH_2Cl_2, rt, 12 h, 74%; (e) Et_3SiH, $BF_3{\cdot}OEt_2/CH_2Cl_2$, 0 °C to rt, 4 h, 99%; (f) LevOH, EDC, DMAP/CH_2Cl_2, rt, 12 h, 94%; (g) NBS, H_2O/acetone, −25 °C, 1 h, 98%; (h) CCl_3CN, DBU/CH_2Cl_2, rt, 2 h, 81%; (i) **5**, TMSOTf/CH_2Cl_2, 3 Å MS, −25 °C, 0.5 h, 60%.

to afford compound **11**. The 4,6-benzylidene group of **11** was reductively opened[29] using Et_3SiH and $BF_3{\cdot}OEt_2$ in DCM to give 6′-OBn compound **12**, and then the 4-OH of **12** was protected with a levulinoyl group to give **13**. Subsequently, compound **13** was subjected to hydrolysis with *N*-bromosuccinimide (NBS) in acetone and water, followed by treatment with trichloroacetonitrile and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to give the fully protected glycosyl trichloroacetimidate **14**. Straightforward glycosylation of chlorgenin with **14** using TMSOTf in DCM having 3 Å MS afforded the core structure 3-β-*O*-glucopyranosides **4** in 60% yield and with complete selectivity for the beta diastereomers, as moved by NMR.

To expand the saponin library, nine sugars (L-arabinose, L-fucose, L-xylose, D-xylose, D-mannose, D-glucose, D-galactose, D-lactose, and L-rhamnose) were selected for combinatorial glycosylation at the 2′ and 4′ positions of **4**. These were elaborated to the corresponding series of glycosyl trichloroacetimidate donors **15**–**23** according to the general procedure depicted in Scheme 5.

Compounds bearing a di-(α-L-rhamnopyranosyl) moiety attached at 2′- or 4′-position of 3-glucosyl-diosgenin, such as dichomin, was reported to exhibit various biological activities.[30] To further evaluate the role of rhamnose in the biological activity, bis(α-L-rhamnopyranosyl donor **24** was also synthesized (Scheme 6). After protection of **25** by 2,2-dimethoxyl propane (2,2-DMP) to give 2,3-*O*-acetonide **26**, and after glycosylation of

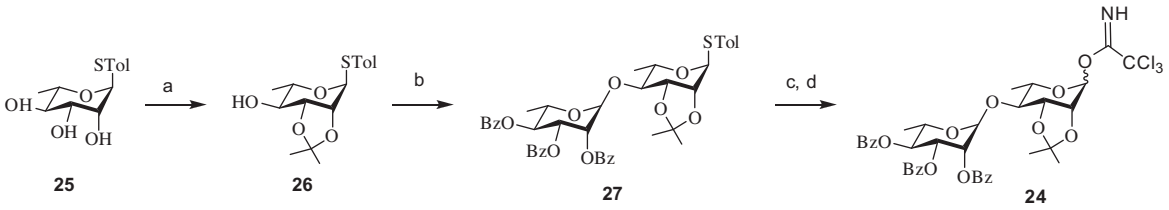


Scheme 5. General preparation of glycosyl trichloroacetimidate donors (a) BzCl, DMAP/pyridine, 0 °C to rt, 5 h; (b) *p*-toluenethiol, $BF_3{\cdot}OEt_2/CH_2Cl_2$, 0 °C to rt, 8 h; (c) NBS, H_2O/acetone, −25 °C, 1 h, 98%; (d) CCl_3CN, DBU/CH_2Cl_2, rt, 2 h, 81%.

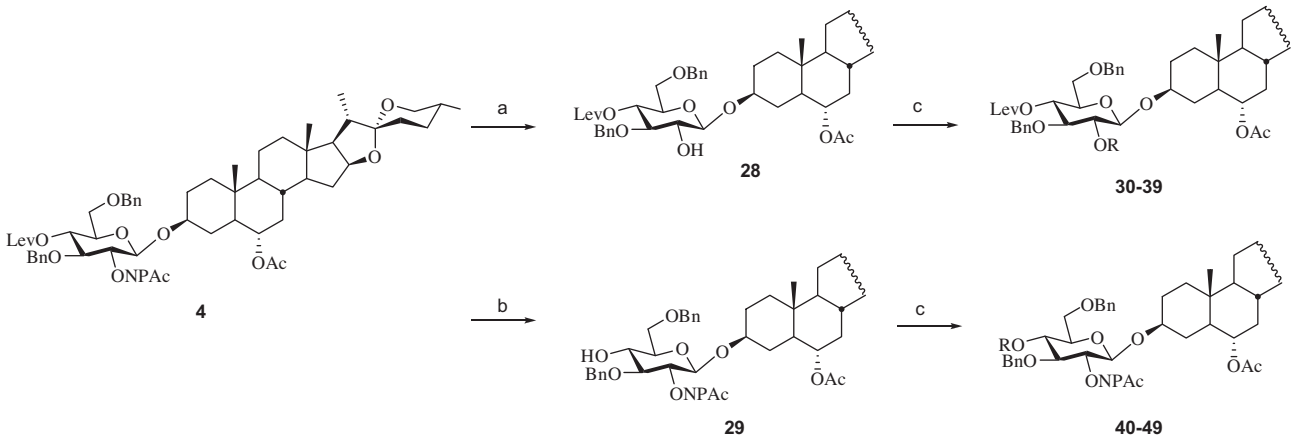
26 with compound **23**, was then converted to glycosyl trichloroacetimidate **24** by successively treating with NBS in aqueous acetone and CCl_3CN and DBU.

With the core **4** as a glycosyl acceptor and 10 glycosyl donors **15**–**24** in hand, orthogonal removal of the 4′-*O*-levulinoyl group using hydrazine acetate and of the 2′-*O*-2-nitrophenylacetyl group using Zn/NH_4Cl afforded compounds **28** and **29**, respectively (Scheme 7). Compounds **28** and **29** were then glycosylated with various glycosyl donors **15**–**24** in CH_2Cl_2 at −25 °C using TMSOTf as a promoter to give compounds **30**–**39** with β(1→2) linkage and **40**–**49** with β(1→4) linkage, respectively. In addition, the 3′-OLev group of compound **48** was removed using hydrazine and the product glycosylated with glycosyl trichloroacetimidates **23** and **24** to afford **51** and **52**, respectively (Scheme 8). Finally, compounds **4**, **30–38, 40–48**, and **51** were subjected to hydrolysis using LiOH in THF/MeOH followed by Pd-catalyzed hydrogenolysis to give desired products **53–62** and **2**, **64–72**. Compounds **39**, **49**, and **52** required additional hydrolysis of the acetonide by acetic acid, followed by global deprotection methods to afford products **63**, **73**, and **74** (Scheme 9).

The in vitro activities of the chlorogenin derivatives (**2**, **53**–**74**) against the leukemia cell CCRF were evaluated using the tetrazolium dye (MTT) assay.[31] Dioscin, as a positive control, showed an IC_{50} of 2.5 μM, but the chlorogenin derivatives synthesized displayed significantly reduced activities. Compounds bearing L-fucosyl-, D-galactosyl-, or D-lactosyl, L-rhamnosyl-, and 4-*O*-(α-L-rhamnosyl)-α-L-rhamnosyl at the 2′OH of 3-*O*-β-glycosyl-chlorogenin (**55**, **60**, **61**, **62**, **63**) displayed weak anti-tumor activities, inhibiting 20–40% cell growth at a concentration of 10 μM; however, their GI_{50} was all over 30 μM. Similar results were seen in assays against leukemia cell line HL-60 and human prostate carcinoma PC-3, leading us to conclude that chacotriosyl glycoside moiety is essential for cytotoxicity. The ability of these compounds to block the entry of the H5N1 influenza virus was also evaluated; no inhibitory activity was found. The inconsistent nature of our results to the literature might be due to the differing assay conditions; this is currently being investigated, and results will be reported in due course.



Scheme 6. Reagents and conditions: (a) 2,2-DMP, acetone, CSA, rt, 15 h, 72%; (b) **23**, TMSOTf/CH_2Cl_2, 3 Å MS, −25 °C, 0.5 h, 68%; (c) NBS, H_2O/acetone, -25 °C, 1 h, 98%; (d) CCl_3CN, DBU/CH_2Cl_2, rt, 2 h, 81%.



30, 40: R= (82%, 89%) **35, 45**: R= (34%, 62%)

31, 41: R= (82%, 45%) **36, 46**: R= (35%, 34%)

32, 42: R= (82%, 55%) **37, 47:** R= (48%, 53%)

33, 43: R= (49%, 57%) **38, 48: R=** (49%, 95%)

34, 44: R= (61%, 70%) **39, 49**: R= (48%, 46%)

Scheme 7. Reagents and conditions: (a) Zn, NH_4Cl/CH_2Cl_2, MeOH, rt, 12 h, 81%; (b) hydrazine acetate/CH_2Cl_2, MeOH, rt, 8 h, 70%; (c) **15–24**, TMSOTf/CH_2Cl_2, 3 Å MS, −25 °C, 0.5 h.

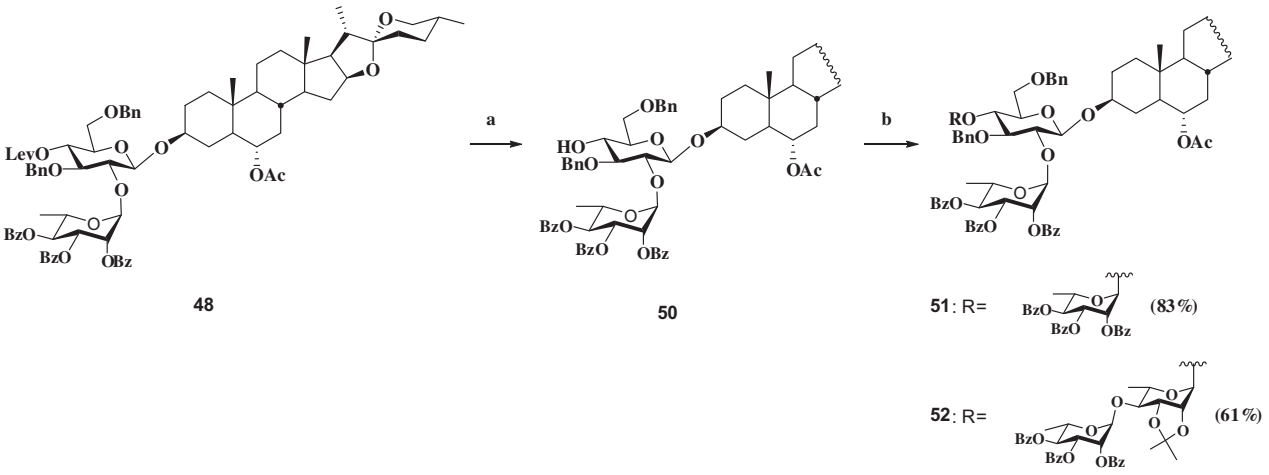
3. Conclusion

An efficient method for the construction of a glycosyl library of chlorogenin 3β-*O*-glucosides has been developed. Both the 2′-OH and 4′-OH groups of chlorogenin 3β-*O*-glucoside were glycosylated with 10 different glycoside donors to afford di-, tri-, and tetra-saccharides corresponding to chlorogenin glycosides. All these compounds were subjected to anti-cytotoxic, and anti-influenza entry assays, but none showed potent activity, suggesting that the unique 2′,4′-di-*O*-rhamnosyl moiety of dioscin is essential for activity. It is thought that our method, using orthogonal approach to efficiently construct more than 20 derivatives of dioscin is useful to investigate the SAR of bioactive glucose-conjugated compounds.

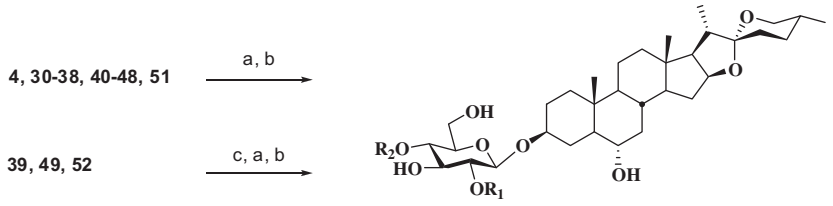
4. Experimental

4.1. General methods

Reactions were monitored by thin-layer chromatography (Merck, silica gel 60F-254) using *p*-anisaldehyde or cerium molybdate as the stain reagent. Silica gel used for flash column chromatography was Mallinckrodt type 60 (230–400 mesh). Unless otherwise noted, reagents and materials were obtained from commercial sources and used as provided without further purification. ^1H and ^{13}C NMR spectra were recorded on a Bruker AV-400 or AVII-600-Cry spectrometer and referenced to residual solvent peaks ($CDCl_3$: ^1H $\delta = 7.24$, ^{13}C $\delta = 77.0$; [D_4] MeOH: ^1H $\delta = 3.30$, ^{13}C



Scheme 8. Reagents and conditions: (a) hydrazine acetate/CH_2Cl_2, MeOH, rt, 8 h, 78%; (b) **23** or **24** TMSOTf/CH_2Cl_2, 3 Å MS, −25 °C, 0.5 h.



53: R_1 = H, R_2 = H (58%)

54: R_1 = β-L-arabinose, R_2 = H (41%)

55: R_1 = β-L-fucose, R_2 = H (50%)

56: R_1 = β-L-xylose, R_2 = H (60%)

57: R_1 = β-D-xylose, R_2 = H (45%)

58: R_1 = α-D-mannose, R_2 = H (88%)

59: R_1 = β-D-glucose, R_2 = H (63%)

60: R_1 = β-D-galactose, R_2 = H (49%)

61: R_1 = β-D-lactose, R_2 = H (42%)

62: R_1 = α-L-rhamnose, R_2 = H (70%)

63: R_1 = α-4-*O*-(L-rhamnose)-L-rhamnose, R_2 = H (42%)

64: R_1 = H, R_2 = β-L-arabinose (43%)

65: R_1 = H, R_2 = β-L-fucose (65%)

66: R_1 = H, R_2 = β-L-xylose (60%)

67: R_1 = H, R_2 = β-D-xylose (40%)

68: R_1 = H, R_2 = α-D-mannose (45%)

69: R_1 = H, R_2 = β-D-glucose (45%)

70: R_1 = H, R_2 = β-D-galactose (42%)

71: R_1 = H, R_2 = β-D-lactose (32%)

72: R_1 = H, R_2 = α-L-rhamnose (62%)

2: α-L-rhamnose, R_2 = α-L-rhamnose (73%)

73: R_1 = H, R_2 = α-4-*O*-(L-rhamnose)-L-rhamnose (41%)

74: R_1 = R_1 = α-L-rhamnose, R_2 = α-4-*O*-(L-rhamnose)-L-rhamnose (31%)

Scheme 9. Reagents and conditions: (a) LiOH/THF/MeOH (3:1), rt, 12 h; (b) H_2, Pd/C, rt, 12 h; (c) 80% AcOH, 60 °C, 24 h.

δ = 49). Exact mass measurements were performed on VG platform electrospray ESI/MS or BioTOF II (Taiwan).

4.2. Cell culture and cytotoxic assay

Leukemia cell line CCRF, HL-20, and human prostate carcinoma cell line PC-3 were obtained from the American Type Culture Collection (Rockville, MD). Cells were cultured in RPMI 1640 medium with 10% FBS (v/v) and penicillin (100 U/mL)/streptomycin (100 μg/mL). Cultures were maintained in a humidified incubator at 37 °C in 5% CO_2/95% air. Cells were incubated in the absence or presence of the compounds for the indicated concentrations and times, and then the mitochondrial MTT reduction activity was assessed. MTT was dissolved in PBS at a concentration of 5 mg/mL and filtered. From the stock solution, 10 μL per 100 μL of medium was added to each well, and plates were gently shaken and incubated at 37 °C for 1 h. After the loading of MTT, the medium was replaced with 100 μL acidified β-isopropanol and left for 5–10 min at rt for color development. The plate was read by enzyme-linked immunosorbent assay reader (570 nm) to get the absorbance density values.

4.3. Synthesis and characterization of compounds

4.3.1. 3β-*O*-Benzylchlorogenin (6)

NaH (5.8 g, 144.7 mmol) was slowly added to a solution of diosgenin (30 g, 72.3 mmol) in THF/DMF (1:1, 500 mL) at 0 °C, with stirring. After 10 min, benzyl chloride (16.7 mL, 144.7 mmol) was

added, and the solution was maintained at 60 °C for 15 h. The reaction mixture was diluted with methanol and CH_2Cl_2 and was washed subsequently with water and satd $NaHCO_3$. The organic layer was dried over $MgSO_4$, filtered, and concentrated to obtain the crude products, which were purified by recrystallization from $CHCl_3$ to afford 3β-*O*-benzyldiosgenin. A solution of 1.0 N BH_3 in THF (89.1 mL, 89.1 mmol) was added slowly to a solution of 3β-*O*-benzyldiosgenin (15.0 g, 29.7 mmol) in dry THF (200 mL) under nitrogen at 0 °C. The mixture was warmed to rt and stirred overnight. 10 N NaOH (18.5 mL, 185 mmol) was added over 30 min at 0 °C, followed by addition of 30% H_2O_2 (18.2 mL, 13 mmol), and vigorous stirring was continued at rt for 2 h. The mixture was diluted with CH_2Cl_2 and washed with 1.0 N HCl, satd $NaHCO_3$, and brine, and dried over $MgSO_4$, filtered, and concentrated in vacuum. The residue was column chromatographed on silica gel EtOAc/hexane, 1:2) to give **6** (12 g, 32%) as white solid: mp 186–190 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.25–7.14 (m, 5H, H-Ar), 4.50 (d, J = 11.7 Hz, 1H, CH_2 of Bn), 4.43 (d, J = 12.0 Hz, 1H, CH_2 of Bn), 4.30 (dd, J = 7.5, 15.0 Hz, 1H, H-16), 3.39–3.18 (m, 4H, H-6, H-3, H-26a, H-26b), 2.27 (d, J = 12.3 Hz, 1H, OH), 1.89–1.88 (m, 2H), 1.79–1.78 (m, 3H), 1.70–1.48 (m, 9H), 1.39–1.38 (m, 3H), 1.22–0.98 (m, 5H), 0.87–0.86 (m, 5H), 0.73 (s, 3H, H-19), 0.70 (d, J = 6.2 Hz, 3H, H-27), 0.67 (s, 3H, H-18), 0.57–0.56 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 138.9, 128.2, 127.4, 127.2, 109.1 (C-22), 80.6 (C-16), 77.84 (C-6), 69.83 (CH_2 of Bn), 69.1 (C-3), 66.7 (C-26), 62.0, 55.8, 53.7, 51.4, 41.7, 41.5, 40.4, 39.7, 37.1, 36.5, 33.7, 31.6, 31.2, 30.1, 28.69, 28.68, 28.0, 20.8, 17.0 (C-27), 16.3 (C-18), 14.4 (C-21), 13.3 (C-19); HRMS (ESI) calcd for $C_{34}H_{51}O_4$ $[M+H]^+$: 523.7663, found: 523.7662.

4.3.2. 6α-*O*-Acetylchlorogenin (5)

Acetic anhydride (3.4 mL, 34.4 mmol) and DMAP (28 mg, 0.23 mmol) were added to a solution of **6** (12.0 g, 23.0 mmol) in pyridine (150 mL) at 0 °C. The mixture was stirred at rt for 2 h, and then concentrated in vacuo. The residue was diluted with CH_2Cl_2 and then extracted with 1.0 N HCl and 1.0 N NaOH for three times. The organic layer was dried over $MgSO_4$, filtered, and concentrated. A suspension of the crude products and Pd–C (1.5 g, 10%) in CH_2Cl_2/ethanol (1:4, 150 mL) was stirred under H_2 for 12 h, filtered, and concentrated. The residue was purified by column chromatography on silica gel (EtOAc/*n*-hexane, 1:2) to afford **5** (10.0 g, 92%) as a off-white solid: mp 230 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 4.68–4.67 (m, 1H, H-6), 4.35 (dd, J = 14.8, 17.2 Hz, 1H, H-16), 3.52–3.51 (m, 1H, H-3), 3.45–3.44 (m, 1H, H-26a), 3.34 (t, J = 10.8 Hz, 1H, H-26b), 2.01 (s, 3H, CH_3 of Ac), 1.94–1.93 (m, 2H), 1.82–1.81 (m, 3H), 1.74–1.37 (m, 13H), 1.28–0.97 (m, 6H), 0.93 (d, J = 7.0 Hz, 3H, H-21), 0.86 (s, 3H, H-19), 0.76 (d, J = 6.4 Hz, 3H, H-27), 0.73 (s, 3H, H-18), 0.68–0.67 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 170.7 (OC=O), 109.2 (C-22), 80.6 (C-16), 72.1 (C-6), 70.9 (C-3), 66.8 (C-26), 62.0, 55.9, 53.7, 48.7, 41.6, 40.5, 39.8, 37.7, 37.1, 36.6, 33.7, 32.2, 31.6, 31.3, 31.1, 30.2, 28.7, 21.2 (CH_3 of Ac), 20.9, 17.1 (C-27), 16.4 (C-18), 14.4 (C-21), 13.3 (C-19); HRMS (ESI) calcd for $C_{29}H_{47}O_5$ $[M+H]^+$: 475.3423, found: 475.3429.

4.3.3. *p*-Tolyl 2,4,6-tri-*O*-acetyl-3-*O*-benzyl-1-thio-D-glucopyranoside (8)

The mixture of **7**[28] (65.0 g, 148 mmol) was dissolved in dry CH_2Cl_2 (400 mL) and cooled to 0 °C in an ice bath. *p*-Toluenethiol (27.6 g, 222.4 mmol) and $BF_3{\cdot}OEt_2$ (37.6 mL, 296.5 mmol) were added slowly under N_2 at 0 °C. The reaction mixture was warmed to 25 °C over 8 h. The reaction mixture was diluted with CH_2Cl_2 and extracted three times with 1.0 N NaOH, water, and brine. The organic layers were separated, dried over $MgSO_4$, filtered, concentrated, and recrystallized from ethanol to give **8** (54.0 g, 73%) as a white solid: mp 142 °C; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.37 (d, J = 8.1 Hz, 2H, H-Ar), 7.27–7.25 (m, 3H, H-Ar), 7.19 (d, J = 8.1 Hz, 2H, H-Ar), 7.08 (d, J = 8.1 Hz, 2H, H-Ar), 5.03 (t, J = 9.6 Hz, 1H, H-4), 5.00 (t, J = 9.7 Hz, 1H, H-2), 4.57 (dd, J = 11.6, 15.5 Hz, 2H, CH_2 of Bn), 4.55 (d, J = 10.2 Hz, 1H, H-1), 4.13–4.11 (m, 2H, H-6a, H-6b), 3.69 (t, J = 9.2 Hz, 1H, H-3), 3.58–3.56 (m, 1H, H-5), 2.32 (s, 3H, CH_3 of STol), 2.05 (s, 3H, CH_3 of Ac), 2.02 (s, 3H, CH_3 of Ac), 1.94 (s, 3H, CH_3 of Ac); ^{13}C NMR ($CDCl_3$, 100 MHz,) δ 170.5, 169.26, 169.1 (OC=O), 138.3, 137.6, 133.1, 129.5, 128.4, 128.3, 127.7, 127.6, 86.3 (C-1), 81.4, 75.9, 74.1, 71.2, 69.5, 62.4, 21.0, 20.8, 20.6, 20.6; HRMS (ESI) calcd for $C_{26}H_{30}NaO_8S$ $[M+Na]^+$: 525.1559, found: 525.1552.

4.3.4. *p*-Tolyl 3-*O*-benzyl-1-thio-β-D-glucopyranoside (9)

A catalytic amount of NaOMe (260 mg, 4.77 mmol) was added to a solution of **8** (54.0 g, 107 mmol) in dry methanol (450 mL). After stirring overnight, the mixture was neutralized with amberlite-H^+ resin. The resin was then filtered off and the filtrate was concentrated and then dried in vacuo to obtain **9** (35.0 g, 87%) as a white solid: mp 143 °C; $[\alpha]_D^{25}$ −82.1 (c 0.056, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.29 (d, J = 8.1 Hz, 2H, H-Ar), 7.25–7.14 (m, 5H, H-Ar), 7.01 (d, J = 7.9 Hz, 2H, H-Ar), 4.89 (d, J = 11.7 Hz, 1H, CH_2 of Bn), 4.63 (d, J = 11.7 Hz, 1H, CH_2 of Bn), 4.37 (d, J = 9.1 Hz, 1H, H-1), 3.78 (d, J = 11.7 Hz, 1H, H-4), 3.64 (d, J = 11.3 Hz, 1H, H-2), 3.40 (t, J = 9.1 Hz, 1H, H-3), 3.33–3.3.25 (m, 3H, H-5, H-6a, H-6b), 2.23 (s, 3H, CH_3 of STol); ^{13}C NMR ($CDCl_3$, 100 MHz,) δ 138.7, 138.3, 133.4, 129.9, 128.6, 128.0, 127.3, 88.7 (C-1), 85.0, 79.3, 74.8, 72.5, 70.0, 62.7, 21.1; HRMS (ESI) calcd for $C_{20}H_{24}NaO_5S$ $[M+Na]^+$: 399.1242, found: 399.1240.

4.3.5. *p*-Tolyl 3-*O*-benzyl-4,6-*O*-benzylidene-1-thio-β-D-glucopyranoside (10)

CSA (2.2 g, 9.3 mmol) was added to a solution of **9** (35.0 g, 93.1 mmol) and benzaldehyde dimethyl acetal (42 mL, 288 mmol) in dry acetonitrile (350 mL). The mixture was stirred under nitrogen for 4 h at rt. Then, the mixture was quenched with triethylamine until it had a pH value of 7, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (EtOAc-*n*-hexane, 1:7) to afford **10** (33.0 g, 71 .1 mmol, 76%) as a white solid: mp 110 °C; $[\alpha]_D^{25}$ −31.9 (c 0.09, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.98 (d, J = 7.9 Hz, 1H, H-Ar), 7.50–7.12 (m, 11H, H-Ar), 6.99 (d, J = 8.0 Hz, 2H, H-Ar), 5.43 (s, 1H, CHPh), 4.82 (d, J = 11.6 Hz, 1H, CH_2 of Bn), 4.67 (d, J = 11.6 Hz, 1H, CH_2 of Bn), 4.44 (t, J = 9.8 Hz, 1H, H-1), 4.25 (dd, J = 4.9, 10.6 Hz, 1H, H-6a), 3.65 (t, J = 10.2 Hz, 1H, H-4), 3.55 (dd, J = 8.6, 17.2 Hz, 1H, H-3), 3.50 (t, J = 9.2 Hz, 1H, H-2), 3.36–3.34 (m, 2H, H-6b, H-5), 2.21 (s, 3H, CH_3 of STol); ^{13}C NMR ($CDCl_3$, 100 MHz,) δ 138.7, 138.1, 137.1, 133.8, 133.6, 130.1, 129.78, 129.75, 129.3, 128.9, 128.5, 128.4, 128.4, 128.2, 128.1, 127.8, 127.1, 125.9, 101.2 (CHPh), 88.5 (C-1), 81.6, 81.1, 74.7, 72.0, 70.6, 68.6, 21.1 (CH_3 of STol); HRMS (ESI) calcd for $C_{27}H_{28}NaO_5S$ $[M+Na]^+$: 487.1555, found: 487.1549.

4.3.6. *p*-Tolyl 3-*O*-benzyl-4,6-*O*-benzylidene-2-*O*-(2-nitro)phenylacetyl-1-thio-β-D-glucopyranoside (11)

(2-Nitro)phenylacetic acid (25.7 g, 142 mmol), DCC (15.4 g, 74.6 mmol), and DMAP (2.2 g, 28 mmol) were added to a solution of **10** (33.0 g, 71.1 mmol) in dry CH_2Cl_2 (350 mL) under nitrogen, and stirred overnight at rt. The precipitation formed in this reaction mixture was removed by filtration and the residue was washed with CH_2Cl_2. The filtrate was concentrated in vacuo and then purified by column chromatography on silica gel (toluene/acetone, 95:5) to afford **11** (33.0 g, 74%) as a white solid: mp 164 °C; $[\alpha]_D^{25}$ −31.9 (c 0.1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.93 (d, J = 8.0 Hz, 1H, H-Ar), 7.39 (t, J = 8.0 Hz, 1H, H-Ar), 7.32 (m, 3H, H-Ar), 7.27–7.12 (m, 11H, H-Ar), 6.98 (d, J = 8.0 Hz, 2H, H-Ar), 5.42 (s, 1H, CHPh), 4.87 (t, J = 9.0 Hz, 1H, H-2), 4.70 (d, J = 11.8 Hz, 1H, CH_2 of Bn), 4.49 (d, J = 11.8 Hz, 1H, CH_2 of Bn),

4.48 (d, *J* = 10.0 Hz, 1H, H-1), 4.24 (dd, *J* = 5.0, 10.5 Hz, 1H, H-6a′), 3.94 (d, *J* = 16.6 Hz, 1H, CH_2 of NPAc), 3.87 (d, *J* = 16.6 Hz, 1H, CH_2 of NPAc), 3.64–3.62 (m, 2H, H-6b′, H-3), 3.56 (d, *J* = 9.4 Hz, 1H, H-4), 3.35–3.33 (m, 1H, H-5), 2.21 (s, 3H, CH_3 of STol); ^{13}C NMR ($CDCl_3$, 150 MHz,) δ 168.2 (OC═O), 138.5, 138.1, 137.0, 134.4, 133.6, 133.2, 133.0, 129.6, 128.9–127.5, 125.9, 125.1, 101.1 (*C*HPh), 86.7 (C-1), 81.1 (C-4), 80.0 (C-3), 74.3 (CH_2 of Bn), 72.2 (C-2), 70.40 (C-5), 68.4 (C-6), 39.2 (*C*H_2 of NPAc), 21.1 (*C*H_3 of STol). HRMS (ESI) calcd for $C_{35}H_{33}NO_8SNa$ $[M+Na]^+$: 650.1819, found: 650.1799.

4.3.7. *p*-Tolyl 3,6-di-*O*-benzyl-2-*O*-(2-nitro)phenylacetyl-1-thio-β-D-glucopyranoside (12)

Et_3SiH (93 mL, 574 mmol) and $BF_3{\cdot}Et_2O$ (12 mL, 95.5 mmol) were added to a solution of **11** (34.4 g, 52.9 mmol) in dry CH_2Cl_2 (300 mL) at 0 °C. The reaction mixture was warmed to 25 °C over 4 h. The mixture was diluted with CH_2Cl_2, washed with satd $NaHCO_3$, dried, and concentrated in vacuo. The residue was purified by column chromatography (EtOAc/*n*-hexane, 1:3.5) to provide **12** (33.0 g, 99%) as a off-white solid: mp 100 °C; $[\alpha]_D^{25}$ −19.9 (*c* 0.1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.04 (d, *J* = 8.0 Hz, 1H, H-Ar), 7.52–7.29 (m, 15H, H-Ar), 7.07 (d, *J* = 8.0 Hz, 2H, H-Ar), 5.01 (t, *J* = 9.5 Hz, 1H, H-2), 4.70 (s, 2H, CH_2 of Bn), 4.57 (d, *J* = 10.0 Hz, 1H, H-1), 4.55 (dd, *J* = 11.9, 18.4 Hz, 2H, CH_2 of Bn), 4.07–4.06 (m, 2H, CH_2 of NPAc), 3.80–3.72 (m, 2H, H-6a′, H-6b′), 3.64 (t, *J* = 9.3 Hz, 1H, H-4), 3.54 (t, *J* = 9.0 Hz, 1H, H-3), 3.50–3.46 (m, 1H, H-5), 2.31 (s, 3H, CH_3 of STol); ^{13}C NMR ($CDCl_3$, 150 MHz,) δ 168.3 (OC═O), 148.8, 138.1, 137.8, 137.7, 133.1, 133.0, 129.3, 128.84–127.47, 124.9, 86.0 (C-1), 83.6 (C-3), 78.3 (C-5), 74.3 (CH_2 of Bn), 73.3 (CH_2 of Bn), 72.2 (C-2), 71.0 (C-4), 69.8 (C-6), 39.1 (*C*H_2 of NPAc), 20.9 (*C*H_3 of STol); HRMS (ESI) calcd for $C_{35}H_{35}NO_8S$-Na $[M+Na]^+$: 652.1976, found: 652.1956.

4.3.8. *p*-Tolyl 3,6-di-*O*-benzyl-4-*O*-levulinoyl-2-*O*-(2-nitro)phenylacetyl-1-thio-β-D-glucopyranoside (13)

LevOH (53.8 mL, 524 mmol), EDC (40.6 g, 262 mmol), and DMAP (82.8 mg, 1.00 mmol) were added to a solution of compound **12** (33.0 g, 52.4 mmol) in dry CH_2Cl_2 (350 mL) under nitrogen. The solution was stirred overnight at rt. The reaction mixture was diluted with CH_2Cl_2, filtered, and the filtrate was washed with water and brine. The organic layers were separated and dried over $MgSO_4$ and then filtered. The filtrate was concentrated under vacuum to obtain the crude products, recrystallized from methanol to give **13** (36 g, 94%) as a white solid: mp 137 °C; $[\alpha]_D^{25}$ −12.5 (*c* 0.04, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.03 (d, *J* = 8.0 Hz, 1H, Ar-H), 7.51 (t, *J* = 7.4 Hz, 1H, Ar-H), 7.43 (t, *J* = 7.7 Hz, 1H, H-Ar), 7.36 (d, *J* = 8.0 Hz, 2H, Ar-H), 7.33–7.23 (m, 9H, H-Ar), 7.19 (d, *J* = 7.2 Hz, 2H, H-Ar), 6.99 (d, *J* = 8.0 Hz, 2H, H-Ar), 4.98–4.97 (m, 2H, H-2, H-4), 4.56 (d, *J* = 11.7 Hz, 1H, CH_2 of Bn), 4.54 (d, *J* = 10.2 Hz, 1H, H-1), 4.50 (d, *J* = 11.6 Hz, 1H, CH_2 of Bn), 4.48 (dd, *J* = 14.1, 11.7 Hz, 2H, CH_2 of Bn), 4.03 (d, *J* = 16.7 Hz, 1H, C*H* of NPAc), 3.98 (d, *J* = 16.7 Hz, 1H, C*H* of NPAc), 3.69 (t, *J* = 9.1 Hz, 1H, H-3), 3.57–3.55 (m, 3H, H-5, H-6a′, H-6b′), 2.58–2.51 (m, 2H, CH_2 of Lev), 2.37–2.27 (m, 2H, CH_2 of Lev), 2.27 (s, 3H, CH_3 of STol), 2.08 (s, 3H, CH_3 of Lev); ^{13}C NMR ($CDCl_3$, 150 MHz,) δ 206.1 (C═O), 171.4, 168.2 (OC═O), 149.1, 138.1, 138.1, 138.1, 133.3, 133.1 (C-Ar), 129.6, 128.89–127.54, 125.1 (CH-Ar), 86.2 (C-1), 81.6 (C-3), 77.7 (C-5), 74.0 (CH_2 of Bn), 73.5 (CH_2 of Bn), 72.4 (C-2), 70.7 (C-4), 69.6 (C-6), 39.2 (CH_2 of NPAc), 37.6 (CH_2 of Lev), 29.7 (CH_3 of Lev), 27.7 (CH_2 of Lev), 21.1 (CH_3 of STol); HRMS (ESI) calcd for $C_{40}H_{41}NO_{10}SNa$ $[M+Na]^+$: 750.2343, found: 750.2319.

4.3.9. 3,6-Di-*O*-benzyl-4-*O*-levulinoyl-2-*O*-(2-nitro)phenylacetyl-β-D-glucopyranose (14)

NBS (1.78 g, 8.65 mmol) was added to a stirred solution of **13** (36.1 g, 49.5 mmol) in acetone (460 mL) and water (40 mL) at −25 °C. The reaction mixture was continuously stirred at −25 °C for 1 h. It was quenched by satd $NaHCO_3$ and 1.0 N $Na_2S_2O_3$ until the color of the mixture changed from yellow to white. The solution was diluted with CH_2Cl_2 and washed sequentially with water and brine, dried over MgSO4, filtered, and concentrated. The crude mixture was purified by column chromatography (EtOAc/*n*-hexane, 1:2) to afford **14** (30 g, 98%) as a off-white solid: mp 108 °C; $[\alpha]_D^{25}$ +48.1 (*c* 0.2, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.04 (d, *J* = 8.1 Hz, 1H, Ar-H), 7.50 (t, *J* = 7.5 Hz, 1H, Ar-H), 7.41–7.24 (m, 12H, H-Ar), 5.46–5.44 (m, 1H, H-1), 5.09 (t, *J* = 9.7 Hz, 1H, H-4), 4.90 (dd, *J* = 3.4, 10.0 Hz, 1H, H-2), 4.62 (d, *J* = 11.9 Hz, 1H, CH_2 of Bn), 4.55 (d, *J* = 11.9 Hz, 1H, CH_2 of Bn), 4.51 (s, 2H, CH_2 of Bn), 4.18 (m, 1H, H-5), 4.08 (t, *J* = 9.6 Hz, 1H, H-3), 4.02 (d, *J* = 17.1 Hz, 1H, CH_2 of NPAc), 3.94 (d, *J* = 17.1 Hz, 1H, C*H* of NPAc), 3.53–3.52 (m, 2H, H-6a′, H-6b′), 2.60–2.55 (m, 2H, CH_2 of Lev), 2.39–2.30 (m, 2H, CH_2 of Lev), 2.10 (s, 3H, CH_3 of Lev); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 206.3 (*C*═O), 171.1, 169.0 (O*C*═O), 148.0, 138.2, 137.4, 133.4, 132.9, 129.0, 128.3, 127.9–127.0, 124.8, 89.5 (C-1), 76.5 (C-3), 74.1 (CH_2 of Bn), 74.0 (C-2), 73.0 (CH_2 of Bn), 70.4 (C-4), 68.6 (C-6), 68.0 (C-5), 39.2 (CH_2 of NPAc), 37.3 (CH_2 of Lev), 29.3 (CH_3 of Lev), 27.5 (CH_2 of Lev); HRMS (ESI) calcd for $C_{33}H_{35}NO_{11}Na$ $[M+Na]^+$: 644.2102, found: 644.2083.

4.3.10. Chlorogenin 3β-*O*-{3,6-di-*O*-benzyl-4-*O*-levulinoyl-2-*O*-(2-nitro)phenylacetyl]-β-D-glucopyranoside} 6α-acetate (4)

To a solution of **14** (30.0 g, 48.3 mmol) in dry CH_2Cl_2 (300 mL) were added CCl_3CN (24.1 mL, 241 mmol) and DBU (3.6 mL, 24.1 mmol). After stirred for 2 h, the mixture was concentrated and purified by column chromatography (EtOAc/hexane, 1:4) to obtain imidated intermediate (30.0 g, 81%) as yellow oil. The imidate (30.0 g, 39.2 mmol) and acceptor **5** (10.3 g, 21.7 mmol) in CH_2Cl_2 (400 mL) were stirred in the presence of 3 Å molecular sieves (10 g, powdered) for 10 min. The mixture was cooled to −25 °C and TMSOTf (787 μL, 4.3 mmol) was added. After stirred at −25 °C for 30 min, the solution was quenched by triethylamine to adjust the pH value to be around 7. The solution was filtered, concentrated, and purified by column chromatography (EtOAc/hexane, 1:3) to afford **4** (14.1 g, 60%) as a off-white solid: mp 193 °C; $[\alpha]_D^{25}$ −11.9 (*c* 0.05, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.27 (d, *J* = 7.8 Hz, 1H, H-Ar), 7.98 (d, *J* = 7.6 Hz, 1H, H-Ar), 7.70–7.69 (m, 1H, H-Ar), 7.58–7.56 (m, 1H, H-Ar), 7.30–7.13 (m, 10H, H-Ar), 5.05 (t, *J* = 9.4 Hz, 1H, H-4′), 5.03 (t, *J* = 8.4 Hz, 1H, H-2′), 4.81 (d, *J* = 11.5 Hz, 1H, CH_2 of Bn), 4.67 (d, *J* = 7.6 Hz, 1H, H-1′), 4.64–4.62 (m, 1H, H-6), 4.52 (d, *J* = 11.3 Hz, 1H, CH_2 of Bn), 4.51 (s, 2H, CH_2 of Bn), 4.36–4.33 (m, 1H, H-16), 3.85 (t, *J* = 9.0 Hz, 1H, H-3′), 3.63–3.51 (m, 6H, H-3, H-5′, H-6a′, H-6b′, CH_2 of NPAc), 3.45–3.44 (m, 1H, H-26a), 3.35 (t, *J* = 10.9 Hz, 1H, H-26b), 2.57–2.53 (m, 2H, CH_2 of Lev), 2.45–2.15 (m, 2H, CH_2 of Lev), 2.08 (s, 3H, CH_3 of Lev), 2.01 (s, 3H, CH_3 of Ac), 1.91–1.90 (m, 4H), 1.73–1.52 (m, 13H), 1.29–1.06 (m, 8H), 0.94 (d, *J* = 7.0 Hz, 3H, H-21), 0.85 (s, 3H, H-19), 0.77 (d, *J* = 6.3 Hz, 3H, H-27), 0.74 (s, 3H, H-18), 0.60–0.58 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 206.15 (*C*═O), 171.5, 170.6, 162.9 (O*C*═O), 146.5, 138.1, 138.0, 132.8, 131.1, 131.1, 130.3, 129.0, 128.3–127.2, 125.9, 109.2 (C-22), 98.7 (C-1′), 80.6 (C-16), 79.7 (C-3′), 78.4 (C-3), 76.8 (C-2′), 73.6 (CH_2 of Bn), 73.6 (CH_2 of Bn), 73.4 (C-5′), 72.3 (C-6), 70.8 (C-4′), 69.7 (C-6′), 66.8 (C-26), 62.0, 55.9, 53.7, 48.5, 41.5, 40.5, 39.8 (CH_2 of NPAc), 37.8, 37.6, 37.0, 36.7, 33.6, 31.6, 31.3, 30.2, 29.7 (CH_3 of Lev), 28.9, 28.7, 28.2, 27.6, 21.4, 21.3 (CH_3 of Ac), 20.8, 17.1 (C-27), 16.3 (C-18), 14.4 (C-21), 13.2 (C-19); HRMS (ESI) calcd for $C_{62}H_{79}NO_{15}Na$ $[M+Na]^+$: 1100.5342, found: 1100.5353.

4.3.11. Chlorogenin 3β-*O*-(3,6-di-*O*-benzyl-4-*O*-levulinoyl-β-D-glucopyranoside) 6α-acetate (28)

Activated Zn powder (1.8 g, 27.8 mmol) and NH_4Cl (893 mg, 16.7 mmol) were added to a solution of **4** (6.0 g, 5.6 mmol) in

CH_2Cl_2/methanol (1:1, 70 mL). The solution was stirred at rt overnight. The reaction mixture was filtered, washed with methanol, and the filtrate was concentrated. The residue was purified by column chromatography (toluene/acetone, 15:1) to afford **28** (4.1 g, 81%) as yellow oil: $[\alpha]_D^{25}$ −37.6 (*c* 0.09, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.27–7.17 (m, 10H, H-Ar), 4.87–4.86 (m, 1H, H-4′), 4.75–4.74 (m, 1H, C*H*$_2$ of Bn), 4.62–4.61 (m, 2H, H-6, C*H*$_2$ of Bn), 4.45–4.44 (m, 2H, C*H*$_2$ of Bn), 4.31–4.28 (m, 2H, H-1′, H-16), 3.52–3.47 (m, 6H, H-3, H-5′, H-3′, H-6a′, H-6b′, H-2′), 3.39–3.38 (m, 1H, H-26a), 3.29–3.28 (m, 1H, H-26b), 2.59–2.46 (m, 2H, C*H*$_2$ of Lev), 2.37–2.24 (m, 2H, C*H*$_2$ of Lev), 2.05 (s, 3H, C*H*$_3$ of Lev), 1.98 (s, 3H, C*H*$_3$ of Ac), 1.85–1.84 (m, 5H), 1.70–1.35 (m, 13H), 1.24–1.05 (m, 7H), 0.89 (s, 3H, H-21), 0.81 (s, 3H, H-19), 0.72 (d, *J* = 6.2 Hz, 3H, H-27), 0.68 (s, 3H, H-18), 0.60–0.58 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 206.1 (*C*=O), 171.6, 170.6, (O*C*=O), 138.4, 138.1, 128.3–127.5, 109.1 (C-22), 101.2 (C-1′), 81.4 (C-3′), 80.5 (C-16), 78.6 (C-3), 74.2 (C-2′), 74.1 (*C*H$_2$ of Bn), 73.5 (C-5′), 73.4 (*C*H$_2$ of Bn), 72.2 (C-6), 70.9 (C-4′), 69.7 (C-6′), 66.8 (C-26), 62.0, 55.9, 53.6, 48.4, 41.5, 40.5, 39.7, 37.7, 37.6, 37.0, 37.6 (*C*H$_2$ of Lev), 36.6, 33.6, 31.6, 31.2, 29.7 (*C*H$_3$ of Lev), 29.1, 28.7, 28.7, 27.8 (*C*H$_2$ of Lev), 21.3 (*C*H$_3$ of Ac), 20.8, 17.0 (*C*-27), 16.3 (C-18), 14.4 (C-21), 13.2 (C-19); HRMS (ESI) calcd for $C_{54}H_{74}O_{12}Na$ $[M+Na]^+$: 937.5072, found: 937.5051.

4.3.12. Chlorogenin 3β-*O*-(3,6-di-*O*-benzyl-2-*O*-(2-nitro)phenylacetyl-β-D-glucopyranoside) 6α-acetate (29)

Hydrazine acetate (1.0 g, 10.9 mmol) was added to a solution of **164** (6.0 g, 5.6 mmol) in CH_2Cl_2/methanol (1:1, 70 mL). After stirred for 8 h, the mixture was concentrated in vacuo and the residue was purified by column chromatography (EtOAc/hexane, 1:3) to afford **176** (3.8 g, 3.9 mmol, 70%) as yellow oil: $[\alpha]_D^{25}$ −10.5 (*c* 0.057, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.28 (d, *J* = 8.2 Hz, 1H, H-Ar), 7.98 (d, *J* = 8.1 Hz, 1H, H-Ar), 7.70 (t, *J* = 7.9 Hz, 1H, H-Ar), 7.58 (t, *J* = 7.9 Hz, 1H, H-Ar), 7.33–7.24 (m, 10H, H-Ar), 4.96 (t, *J* = 7.8 Hz, 1H, H-2′), 4.90 (d, *J* = 11.7 Hz, 1H, C*H*$_2$ of Bn), 4.62–4.60 (m, 3H, H-1′, H-6, C*H*$_2$ of Bn), 4.57 (d, *J* = 12.1 Hz, 1H, C*H*$_2$ of Bn), 4.53 (d, *J* = 12.1 Hz, 1H, C*H*$_2$ of Bn), 4.35 (dd, *J* = 14.6, 7.3 Hz, 1H, H-16), 3.75–3.58 (m, 5H, H-3′, H-4′, H-6a′, H-6b′, C*H* of NPAc), 3.53–3.51 (m, 1H, H-3), 3.45–3.44 (m, 2H, C*H* of NPAc, H-26a), 3.35 (d, *J* = 10.7 Hz, 1H, H-26b), 2.01 (s, 3H, C*H*$_3$ of Ac), 1.99–1.58 (m, 12H), 1.51–1.40 (m, 3H), 1.28–0.95 (m, 10H), 0.93 (d, *J* = 7.0 Hz, 3H, H-21), 0.84 (s, 3H, H-19), 0.77 (d, *J* = 6.2 Hz, 3H, H-27), 0.73 (s, 3H, H-18), 0.64 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 170.6, 168.1 (O*C*=O), 138.3, 137.7, 133.2, 132.9, 131.1, 128.6–127.6, 125.1, 109.2 (C-22), 98.9 (C-1′), 82.4 (C-3′), 80.6 (C-16), 74.4 (C-3), 74.2 (C-4′), 74.1 (*C*H$_2$ of Bn), 73.9 (C-5′), 73.6 (*C*H$_2$ of Bn), 73.6 (C-6), 72.3 (C-2′), 72.1 (C-6′), 71.9 (C-26), 66.8, 62.0, 55.9, 53.6, 48.6, 48.3, 41.5, 40.5, 39.7, 39.2 (*C*H$_2$ of NPAc), 37.8, 37.1, 36.7, 33.6, 31.6, 31.3, 30.2, 28.7, 21.3 (*C*H$_3$ of Ac), 20.8, 17.0 (C-27), 16.3 (C-18), 14.4 (C-21), 13.2 (C-19); HRMS (ESI) calcd for $C_{57}H_{73}NO_{13}Na$ $[M+Na]^+$: 1002.4974, found: 1002.4935.

4.3.13. General procedure for glycosylation reaction (compounds 30–49, 51–52)

A glycosyl trichloroacetimidate donor was readily prepared by treatment of related 1-hydroxyl sugar (1 mmol = 1 equiv) in dry CH_2Cl_2 (5–20 mL) with trichloroacetonitrile (5 mmol = 5 equiv) and DBU (0.5 mmol = 0.5 equiv). The solution was stirred for 2 h and concentrated and the residue was purified by column chromatography to get glycosyl trichloroacetimidate donors (**15–24**). Then, glycosyl trichloroacetimidate donor (1.8 mmol = 1.8 equiv) and acceptor (1 mmol = 1 equiv) in dry CH_2Cl_2 (5–20 mL) were stirred in the presence of 3 Å molecular sieves (100–300 mg, powdered) for 10 min. The mixture was cooled to −25 °C and TMSOTf (0.2 mmol, 0.2 equiv) was added. On continuous stirring at −25 °C for 30 min, the solution was quenched with triethylamine to the pH value to be around 7. The solution was filtered, concentrated, and purified by column chromatography.

4.3.14. Chlorogenin 3β-*O*-[2-*O*-(2,3,4-tri-*O*-benzoyl-β-L-arabinopyranosyl)-3,6-di-*O*-benzyl-4-*O*-levulinoyl-β-D-glucopyranoside] 6α-acetate (30)

According to the general procedure for glycosylation, treatment of **28** (90 mg, 0.10 mmol) and **15** (89.5 mg, 0.15 mmol) in CH_2Cl_2 afforded **30** (110 mg, 82%) as a off-white solid: mp 123 °C; $[\alpha]_D^{25}$ +31.9 (*c* 0.05, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.03 (d, *J* = 7.6 Hz, 2H, H-Ar), 7.90 (d, *J* = 7.5 Hz, 2H, H-Ar), 7.78 (d, *J* = 7.6 Hz, 2H, H-Ar), 7.56–6.97 (m, 19H, H-Ar), 5.73 (t, *J* = 7.7 Hz, 1H, H-2″), 5.62–5.60 (m, 1H, H-4″), 5.52 (d, *J* = 8.5 Hz, 1H, H-3″), 5.16 (d, *J* = 6.1 Hz, 1H, H-1″), 4.83 (t, *J* = 7.8 Hz, 1H, H-4′), 4.73 (d, *J* = 12.2 Hz, 1H, C*H*$_2$ of Bn), 4.64 (m, 1H, H-6), 4.61 (d, *J* = 7.7 Hz, 1H, H-1′), 4.48 (s, 2H, C*H*$_2$ of Bn), 4.39 (d, *J* = 12.4 Hz, 1H, C*H*$_2$ of Bn), 4.37 (m, 1H, H-16), 4.36 (m, 1H, H-5a″), 3.84 (d, *J* = 12.8 Hz, 1H, H-5b″), 3.72 (t, *J* = 8.5 Hz, 1H, H-2′), 3.66 (m, 1H, H-3), 3.58 (t, *J* = 8.9 Hz, 1H, H-3′), 3.51–3.44 (m, 4H, H-5′, H-6a′, H-6b′, H-26a), 3.38 (t, *J* = 10.9 Hz, 1H, H-26b), 2.46–2.30 (m, 2H, C*H*$_2$ of Lev), 2.30–2.23 (m, 2H, C*H*$_2$ of Lev), 2.02 (s, 3H, C*H*$_3$ of Lev), 2.00–1.96 (m, 2H), 1.91 (s, 3H, C*H*$_3$ of Ac), 1.84–1.80 (m, 2H), 1.77–1.43 (m, 15H), 1.30–1.10 (m, 6H), 0.95 (d, *J* = 7.0 Hz, 3H, H-21), 0.81 (s, 3H, H-19), 0.77 (d, *J* = 5.9 Hz, 3H, H-27), 0.74 (s, 3H, H-18), 0.65–0.64 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 206.1 (*C*=O), 171.7, 170.6, 165.6, 165.5, 165.2 (O*C*=O), 138.5, 138.2, 133.3, 133.2, 133.0, 129.9–127.0, 109.2 (C-22), 100.6 (C-1″), 100.1 (C-1′), 82.3 (C-3′), 81.4 (C-2′), 80.6 (C-16), 78.2 (C-3), 75.2, 73.4 (*C*H$_2$ of Bn), 73.2 (C-5′), 72.3 (C-6), 71.3 (C-4′), 70.8 (C-3″), 70.5 (C-2″), 69.8 (C-6′), 68.4 (C-4″), 66.8 (C-26), 62.7 (C-5″), 62.1, 55.9, 53.72, 53.4, 48.5, 41.6, 40.5, 39.8, 37.7, 37.5 (*C*H$_2$ of Lev), 37.1, 36.7, 33.6, 31.6, 31.3, 30.3, 29.6 (*C*H$_3$ of Lev), 29.3, 28.7, 28.4, 27.6 (*C*H$_2$ of Lev), 21.2 (*C*H$_3$ of Ac), 17.1 (C-27), 16.4 (C-18), 14.4 (C-21), 13.2 (C-19); HRMS (ESI) calcd for $C_{80}H_{94}O_{19}Na$ $[M+Na]^+$: 1381.6282, found: 1381.6176.

4.3.15. Chlorogenin 3β-*O*-[2-*O*-(2,3,4-tri-*O*-benzoyl-β-L-fucopyranosyl)-3,6-di-*O*-benzyl-4-*O*-levulinoyl-β-D-glucopyranoside] 6α-acetate (31)

According to the general procedure for glycosylation, treatment of **28** (90 mg, 0.10 mmol) and **16** (91.6 mg, 0.15 mmol) in CH_2Cl_2 afforded **31** (111 mg, 82%) as a off-white solid: mp 130 °C; $[\alpha]_D^{25}$ +39.9 (*c* 0.05, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.01 (d, *J* = 8.0 Hz, 2H, H-Ar), 7.96 (d, *J* = 7.9 Hz, 2H, H-Ar), 7.74 (d, *J* = 7.7 Hz, 2H, H-Ar), 7.50–7.20 (m, 19H, H-Ar), 5.77 (dd, *J* = 10.3, 8.0 Hz, 1H, H-2″), 5.66 (d, *J* = 3.3 Hz, 1H, H-4″), 5.45 (dd, *J* = 10.4, 3.4 Hz, 1H, H-3″), 5.31 (d, *J* = 8.0 Hz, 1H, H-1″), 5.11 (d, *J* = 11.2 Hz, 1H, C*H*$_2$ of Bn), 4.88 (t, *J* = 9.4 Hz, 1H, H-4′), 4.75 (d, *J* = 11.2 Hz, 1H, C*H*$_2$ of Bn), 4.66 (td, *J* = 11.1, 4.7 Hz, 1H, H-6), 4.46 (br s, 2H, C*H*$_2$ of Bn), 4.38 (q, *J* = 7.3 Hz, 1H, H-16), 4.28 (d, *J* = 7.9 Hz, 1H, H-1′), 4.04 (q, *J* = 6.5 Hz, 1H, H-5″), 3.94 (t, *J* = 8.5 Hz, 1H, H-2′), 3.59 (t, *J* = 9.1 Hz, 1H, H-3′), 3.51 (d, *J* = 7.8 Hz, 1H, H-6a′), 3.49–3.45 (m, 3H, H-5′, H-6b′, H-26a), 3.36 (t, *J* = 10.9 Hz, 1H, H-26b), 3.21–3.19 (m, 1H, H-3), 2.61–2.54 (m, 2H, C*H*$_2$ of Lev), 2.42–2.37 (m, 2H, C*H*$_2$ of Lev), 2.10 (s, 3H, C*H*$_3$ of Lev), 1.98 (s, 3H, C*H*$_3$ of Ac), 1.93–1.90 (m, 2H), 1.76–1.75 (m, 1H), 1.73–1.43 (m, 14H), 1.29–1.26 (m, 5H), 1.14–1.09 (m, 6H), 0.95 (d, *J* = 6.9 Hz, 3H, H-21), 0.84 (s, 3H, H-19), 0.78 (d, *J* = 6.3 Hz, 3H, H-27), 0.75 (s, 3H, H-18), 0.59–0.55 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 206.2 (*C*=O), 171.6, 170.8, 165.7, 165.4, 165.3 (O*C*=O), 138.5, 138.2, 133.4, 133.1, 133.1, 129.8–127.5, 109.3 (C-22), 102.8 (C-1″), 99.6 (C-1′), 81.0 (C-3), 80.6 (C-16), 79.85 (C-3′), 77.8 (C-2′), 74.2, 73.4 (*C*H$_2$ of Bn), 73.2 (C-5′), 72.5 (C-6), 72.1 (C-3″), 71.1 (C-4″), 70.5 (C-4′), 70.5 (C-2″), 69.8 (C-6′), 69.5 (C-5″), 66.8 (C-26), 62.1, 56.0, 53.8, 48.6, 41.6, 40.6, 39.8, 38.0 (*C*H$_3$ of Lev), 37.7 (*C*H$_2$ of Lev), 36.8, 36.6, 33.6, 31.6, 31.3,

30.3, 29.7, 29.5, 29.4, 28.7, 27.9 (*C*H_2 of Lev), 21.1 (*C*H_3 of Ac), 20.8, 17.1 (C-27), 16.4 (C-18), 16.2 (C-6″), 14.4 (C-21), 13.3 (C-19); HRMS (ESI) calcd for $C_{81}H_{96}O_{19}Na$ $[M+Na]^+$: 1395.6438, found: 1395.6330.

4.3.16. Chlorogenin 3β-*O*-[2-*O*-(2,3,4-tri-*O*-benzoyl-β-L-xylopyranosyl)-3,6-di-*O*-benzyl-4-*O*-levulinoyl-β-D-glucopyranoside] 6α-acetate (32)

According to the general procedure for glycosylation, treatment of **28** (90 mg, 0.1 mmol) and **17** (89.5 mg, 0.15 mmol) in CH_2Cl_2 afforded **32** (110 mg, 82.3%) as a white solid: mp, 116 °C; $[\alpha]_D^{25}$ +7.5 (*c* 0.04, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.99 (d, *J* = 8.0 Hz, 2H, H-Ar), 7.93 (d, *J* = 7.2 Hz, 2H, H-Ar), 7.88 (d, *J* = 7.9 Hz, 2H, H-Ar), 7.56–7.20 (m, 19H, H-Ar), 5.70 (t, *J* = 8.4 Hz, 1H, H-3″), 5.45 (dd, *J* = 6.7, 8.6 Hz, 1H, H-2″), 5.31–5.30 (m, 1H, H-4″), 5.26 (d, *J* = 6.7 Hz, 1H,H-1″), 4.93 (d, 1H, *J* = 11.6 Hz, C*H*$_2$ of Bn), 4.88 (t, *J* = 9.1 Hz, 1H, H-4′), 4.66 (d, *J* = 11.6 Hz, 1H, C*H*$_2$ of Bn), 4.63–4.61 (m, 1H, H-6), 4.45 (br s, 2H, CH_2 of Bn), 4.37–4.33 (m, 2H, H-16, H-5a″), 4.30 (d, *J* = 7.9 Hz, 1H, H-1′), 3.81 (t, *J* = 8.2 Hz, 1H, H-2′), 3.56 (t, *J* = 9.2 or 9.7 Hz, 1H, H-3′), 3.49–3.53 (m, 2H, H-5b″, H-6a′), 3.45–3.40 (m, 3H, H-26a, H-5′, H-6b′), 3.36 (t, *J* = 10.9 Hz, 1H, H-26b), 3.23–3.20 (m, 1H, H-3), 2.60–2.49 (m, 2H,C*H*$_2$ of Lev), 2.37–2.23 (m, 2H,C*H*$_2$ of Lev), 2.09 (s, 6H, CH_3 of Lev, C*H*$_3$ of Ac), 2.06–1.82 (m, 4H), 1.78–1.42 (m, 14H), 1.32–1.06 (m, 4H), 0.95 (d, *J* = 7.0 Hz, 3H, H-21), 0.85–0.84 (m, 3H), 0.81(s, 3H, H-19), 0.78 (d, *J* = 6.3 Hz, 3H, H-27), 0.75 (s, 3H, H-18), 0.58–0.55 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 206.2 (C═O), 171.5, 171.2, 165.52, 165.3, 165.0 (O*C*═O), 149.5, 149.4, 149.2, 138.4, 138.2, 135.6, 135.4, 135.2, 133.3, 133.2, 133.2, 129.8–127.4, 123.3, 123.1, 123.0, 109.2 (C-22), 102.2 (C-1′), 99.8 (C-1″), 80.6 (C-16), 80.33 (C-3), 80.32 (C-3′), 78.1 (C-2′), 74.7 (*C*H_2 of Bn), 73.3 (*C*H_2 of Bn), 73.2 (C-5′), 72.3 (C-6), 71.6 (C-3″), 71.5 (C-2″), 70.8 (C-4′), 69.8 (C-4″), 69.8 (C-6′), 66.8 (C-26), 62.1, 62.0 (C-5″), 56.0, 53.8, 48.4, 41.6, 40.5, 39.8, 38.0, 37.7 (*C*H_2 of Lev), 36.8, 36.61, 33.60, 31.6, 31.5, 31.3, 30.3, 29.7 (*C*H_3 of Lev), 29.3, 29.1, 27.8 (*C*H_2 of Lev), 21.3 (*C*H_3 of Ac), 20.8, 17.1 (C-27), 16.4 (C-18), 14.4 (C-21), 13.2 (C-19); HRMS (ESI) calcd for $C_{80}H_{94}O_{19}Na$ $[M+Na]^+$: 1381.6282, found: 1381.6168.

4.3.17. Chlorogenin 3β-*O*-[2-*O*-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)-3,6-di-*O*-benzyl-4-*O*-levulinoyl-β-D-glucopyranoside] 6α-acetate (33)

According to the general procedure for glycosylation, treatment of **28** (90 mg, 0.10 mmol) and **18** (89.5 mg, 0.15 mmol) in CH_2Cl_2 afforded **33** (66 mg, 49%) as a white solid: mp 121 °C; $[\alpha]_D^{25}$ −26.4 (*c* 0.07, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.98 (d, *J* = 7.1 Hz, 2H, H-Ar), 7.96 (d, *J* = 8.2 Hz, 2H, H-Ar), 7.80 (d, *J* = 7.1 Hz, 2H, H-Ar), 7.53–7.03 (m, 19H, H-Ar), 5.61 (t, *J* = 6.0 Hz, 1H, H-3″), 5.34 (t, *J* = 4.3 Hz, 1H, H-2″), 5.31 (d, *J* = 4.2 Hz, 1H, H-1″), 5.22 (q, *J* = 4.1 Hz, 1H, H-4″), 4.83 (t, *J* = 7.8 Hz, 1H, H-4′), 4.68 (d, *J* = 11.8 Hz, 1H, CH_2 of Bn), 4.63–4.61 (m, 2H, H-6, H-5a″), 4.55 (d, *J* = 7.6 Hz, 1H, H-1′), 4.49 (s, 2H, C*H*$_2$ of Bn), 4.46 (d, *J* = 11.7 Hz, 1H, C*H*$_2$ of Bn), 4.36 (dd, *J* = 6.9, 15.0 Hz, 1H, H-16), 3.78 (dd, *J* = 7.9, 7.7 Hz, 1H, H-2′), 3.68–3.64 (m, 2H, H-3′, H-5b″), 3.60–3.47 (m, 4H, H-3, H-5′, H-6a′, H-6b′), 3.51–3.49 (m, 1H, H-26a), 3.35 (t, *J* = 10.7 Hz, 1H, H-26b), 2.52–2.40 (m, 2H, C*H*$_2$ of Lev), 2.30–2.07 (m, 2H, C*H*$_2$ of Lev), 2.07 (m, 6H, C*H*$_3$ of Lev, C*H*$_3$ of Ac), 1.93–1.83 (m, 5H), 1.76–1.41 (m, 13H), 1.29–1.00 (m, 7H), 0.94 (d, *J* = 6.9 Hz, 3H, H-21), 0.82 (s, 3H, H-19), 0.77 (d, *J* = 6.9 Hz, 3H, H-27), 0.73 (s, 3H, H-18), 0.61–0.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 206.0 (C═O), 171.6, 170.7, 165.4, 165.1, 165.1 (O*C*═O), 138.1, 138.1, 133.3, 133.2, 133.1, 129.8–127.1, 109.2 (C-22), 100.9 (C-1′), 99.0 (C-1″), 83.0 (C-3′), 80.6 (C-16), 79.7 (C-3), 78.3 (C-2′), 75.0, 73.4 (CH_2 of Bn), 73.3 (C-5′), 72.1 (C-6), 71.5 (C-4′), 69.9 (C-2″), 69.8 (C-6′), 69.5 (C-3″), 68.5 (C-4″), 66.8 (C-26), 62.1, 60.4 (C-5″), 55.9, 53.7, 48.5, 41.5, 40.5, 39.8, 37.7, 37.6 (*C*H_2 of Lev), 37.0, 36.6, 33.6, 31.6, 31.3, 30.8, 29.6 (*C*H_3 of Lev), 29.4, 28.8, 28.7, 27.7 (*C*H_2 of Lev), 21.1 (*C*H_3 of Ac), 20.8, 17.0 (C-27), 16.4 (C-18), 14.4 (C-21), 13.3 (C-19); HRMS (ESI) calcd for $C_{80}H_{94}O_{19}Na$ $[M+Na]^+$: 1381.6282, found: 1381.6291.

4.3.18. Chlorogenin 3β-*O*-[2-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-3,6-di-*O*-benzyl-4-*O*-levulinoyl-β-D-glucopyranoside] 6α-acetate (34)

According to the general procedure for glycosylation, treatment of **28** (90 mg, 0.10 mmol) and **19** (109 mg, 0.15 mmol) in CH_2Cl_2 afforded **34** (90 mg, 61%) as a white solid: mp 127 °C; $[\alpha]_D^{25}$ −1.3 (*c* 0.08, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.06 (d, *J* = 8.4 Hz, 2H, H-Ar), 8.01 (d, *J* = 7.1 Hz, 2H, H-Ar), 7.81 (d, *J* = 8.5 Hz, 2H, H-Ar), 7.74 (d, *J* = 8.3 Hz, 2H, H-Ar), 7.54–7.10 (m, 22H, H-Ar), 6.03 (t, *J* = 10.3 Hz, 1H, H-4″), 5.86 (dd, *J* = 2.6, 10.2 Hz, 1H, H-3″), 5.66–5.65 (m, 2H, H-1″, H-2″), 5.10 (t, *J* = 9.4 Hz, 1H, H-4′), 4.92 (d, *J* = 11.5 Hz, 1H, C*H*$_2$ of Bn), 4.84 (d, *J* = 11.5 Hz, 1H, C*H*$_2$ of Bn), 4.64 (d, *J* = 7.6 Hz, 1H, H-1′), 4.57–4.54 (m, 2H, H-5″, H-6), 4.53 (s, 2H, C*H*$_2$ of Bn), 4.35–4.34 (m, 1H, H-16), 4.19 (dd, *J* = 12.2, 1.9 Hz, 1H, H-6a″), 4.00 (dd, *J* = 12.3, 4.3 Hz, 1H, H-6b″), 3.81–3.76 (m, 2H, H-2′, H-3′), 3.63–3.56 (m, 4H, H-5′, H-3, H-6a′, H-6b′), 3.44–3.43 (m, 1H, H-26a), 3.35 (t, *J* = 10.5 Hz, 1H, H-26b), 2.60–2.52 (m, 2H, C*H*$_2$ of Lev), 2.45–2.30 (m, 2H, C*H*$_2$ of Lev), 2.07 (s, 3H, C*H*$_3$ of Lev), 2.04–2.02 (m, 2H), 1.91 (s, 3H, CH_3 of Ac), 1.88–1.81 (m, 4H), 1.75–1.41 (m, 12H), 1.29–1.18 (m, 5H), 1.10–0.93 (m, 2H), 0.94 (d, *J* = 7.0 Hz, 3H, H-21), 0.84 (s, 3H, H-19), 0.77 (d, *J* = 6.3 Hz, 3H, H-27), 0.72 (s, 3H, H-18), 0.65–0.62 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 206.3 (C═O), 171.1, 170.9, 166.8, 166.0, 165.3, 164.7 (O*C*═O), 138.1, 137.6, 133.3, 133.3, 133.2, 132.8, 130.0–127.1, 109.2 (C-22), 101.6 (C-1′), 97.6 (C-1″), 81.0 (C-3′), 80.6 (C-16), 78.9 (C-3), 75.9 (C-2′), 75.3, 73.5 (*C*H_2 of Bn), 73.3 (C-5′), 72.4 (C-5″), 72.2 (C-4′), 70.1 (C-2″), 70.1 (C-3″), 69.7 (C-6′), 68.7 (C-6), 66.8 (C-26), 66.6 (C-4″), 62.4 (C-6″), 62.1, 56.0, 53.8, 48.4, 41.5, 40.5, 39.8, 37.7 (*C*H_2 of Lev), 37.7, 37.2, 36.6, 33.5, 31.6, 31.3, 30.3, 29.6 (CH_3 of Lev), 29.3, 28.7, 28.4, 27.9 (*C*H_2 of Lev), 21.3 (*C*H_3 of Ac), 20.9, 17.1 (C-27), 16.4 (C-18), 14.4 (C-21), 13.1 (C-19); HRMS (ESI) calcd for $C_{88}H_{100}O_{21}Na$ $[M+Na]^+$: 1515.6649, found: 1515.6770.

4.3.19. Chlorogenin 3β-*O*-[2-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl)-3,6-di-*O*-benzyl-4-*O*-levulinoyl-β-D-glucopyranoside] 6α-acetate (35)

According to the general procedure for glycosylation, treatment of **28** (90 mg, 0.10 mmol) and **20** (109.3 mg, 0.15 mmol) in CH_2Cl_2 afforded **35** (50 mg, 34%) as a white solid: mp 112 °C; $[\alpha]_D^{25}$ −1.4 (*c* 0.07, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.02 (d, *J* = 7.2 Hz, 2H, H-Ar), 7.83 (d, *J* = 7.2 Hz, 2H, H-Ar), 7.76 (t, *J* = 7.2 Hz, 4H, H-Ar), 7.50–7.35 (m, 7H, H-Ar), 7.31–7.27 (m, 7H, H-Ar), 7.23–7.18 (m, 7H, H-Ar), 7.00 (d, *J* = 7.2 Hz, 2H, H-Ar), 5.81 (t, *J* = 7.8 Hz, 1H, H-2″), 5.74 (t, *J* = 7.8 Hz, 1H, H-3″), 5.53 (t, *J* = 7.8 Hz, 1H, H-4″), 5.33 (d, *J* = 7.7 Hz, 1H, H-1′), 4.80 (t, *J* = 7.6 Hz, 1H, H-4′), 4.67–4.64 (m, 3H, H-6a″, H6b″, C*H*$_2$ of Bn), 4.56 (d, *J* = 7.9 Hz, 1H, H-1″), 4.47–4.43 (m, 3H, H-3, C*H*$_2$ of Bn), 4.36–4.35 (m, 1H, H-2′), 4.34 (d, *J* = 12 Hz, 1H, C*H*$_2$ of Bn), 4.07–4.04 (m, 1H, H-6a), 3.73–3.67 (m, 3H, H-6, H-3′, H-4′), 3.64–3.63 (m, 1H, H-5′), 3.55 (t, *J* = 10.1 Hz 1H, H-6a′), 3.53–3.44 (m, 5H, H-6b′, H6a″, H6b″, H-26a, H-5″), 3.36 (t, *J* = 10.9, 1H, H-26b), 2.43–2.33 (m, 2H, C*H*$_2$ of Lev), 2.22–2.15 (m, 2H, C*H*$_2$ of Lev), 2.03 (s, 3H, C*H*$_3$ of Lev), 2.02 (s, 3H, C*H*$_3$ of Ac), 1.96–1.84 (m, 6H), 1.76–1.75 (m, 1H), 1.69–1.37 (m, 14H), 1.27–1.03 (m, 4H), 0.94 (d, *J* = 7.0 Hz, 3H, H-21), 0.79 (d, *J* = 6.3 Hz, 3H, H-27), 0.73 (s, 3H, H-19), 0.58 (s, 3H, H-18), 0.65–0.62 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 171.6, 170.7, 166.1, 165.8, 165.1, 165.1, 138.5, 138.2, 133.4, 133.2, 133.1, 129.9, 129.8, 129.7, 129.1, 128.8, 128.4, 128.3, 128.3, 128.1, 127.6, 127.5, 127.2, 127.1, 109.3 (C-22), 100.4 (C-1″), 100.4 (C-1′), 82.4, 81.0, 80.7, 79.0, 75.2, 73.4, 73.1, 73.1, 72.7, 72.4, 72.3, 71.3, 69.8,

69.6, 66.9, 63.1, 62.1, 58.5, 55.9, 53.5, 48.4, 41.6, 40.6, 39.8, 37.6, 36.9, 36.6, 33.6, 31.6, 31.3, 30.3, 29.6, 29.2, 29.2, 28.7, 27.6, 21.5, 20.9, 18.4, 17.1, 16.4, 14.5, 13.3; HRMS (ESI) calcd for $C_{88}H_{100}O_{21}Na$ $[M+Na]^+$: 1515.6649, found: 1515.6680.

4.3.20. Chlorogenin 3β-*O*-[2-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-3,6-di-*O*-benzyl-4-*O*-levulinoyl-β-D-glucopyranoside] 6α-acetate (36)

According to the general procedure for glycosylation, treatment of **28** (90 mg, 0.10 mmol) and **21** (109.3 mg, 0.15 mmol) in CH_2Cl_2 afforded **36** (52 mg, 35%) as a white solid: mp 76 °C; $[\alpha]_D^{25}$ +23.8 (*c* 0.08, CH_2Cl_2); ^1H NMR ($CDCl_3$, 600 MHz) δ 8.07 (d, *J* = 6.8 Hz, 2H, H-Ar), 7.99 (d, *J* = 8.4 Hz, 2H, H-Ar), 7.73 (m, 4H, H-Ar), 7.47–7.15 (m, 22H, H-Ar), 5.99 (d, *J* = 3.6 Hz, 1H, H-4″), 5.82 (dd, *J* = 9.5, 10.2 Hz, 1H, H-2″), 5.52 (dd, *J* = 4.4, 10.2 Hz, 1H, H-3″), 5.33 (d, *J* = 8.5 Hz, 1H, H-1″), 4.81–4.80 (m, 1H, H-4′), 4.74 (d, *J* = 12.5 Hz, 1H, C*H*$_2$ of Bn), 4.67–4.64 (m, 3H, H-6a″, H-1′, H-6), 4.48 (s, 2H, C*H*$_2$ of Bn), 4.41–4.37 (m, 3H, H-16, C*H*$_2$ of Bn, H-6b″), 4.28–4.27 (m, 1H, H-5″), 3.76 (t, *J* = 8.5 Hz, 1H, H-2′), 3.71–3.70 (m, 1H, H-3), 3.62 (t, *J* = 8.3 Hz, 1H, H-3′), 3.50–3.45 (m, 4H, H-5′, H-6a′, H-6b′, H-26a), 3.37 (t, *J* = 11.0 Hz, 1H, H-26b), 2.45–2.29 (m, 2H, C*H*$_2$ of Lev), 2.21–2.15 (m, 2H, C*H*$_2$ of Lev), 2.02 (s, 3H, C*H*$_3$ of Lev), 1.96 (s, 3H, C*H*$_3$ of Ac), 1.95–1.74 (m, 4H), 1.71–1.33 (m, 15H), 1.23–1.21 (m, 4H), 1.01–0.98 (m, 2H), 0.95 (d, *J* = 7.2 Hz, 3H, H-21), 0.83 (s, 3H, H-19), 0.78 (d, *J* = 6.1 Hz, 3H, H-27), 0.73 (s, 3H, H-18), 0.63–0.62 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 206.1 (C=O), 171.6, 170.6, 165.7, 165.55, 165.52, 165.2 (OC=O), 138.6, 138.1, 133.5, 133.2, 133.2, 133.0, 130.0–126.9, 109.2 (C-22), 100.8 (C-1″), 99.8 (C-1′), 82.2 (C-3′), 81.4 (C-2′), 80.6 (C-16), 78.2 (C-3), 75.2, 73.4 (*C*H$_2$ of Bn), 73.1 (C-5′), 72.4 (C-6), 71.9 (C-3″), 71.4 (C-5″), 71.3 (C-4′), 70.5 (C-2″), 69.7 (C-6′), 67.8 (C-4″), 66.8 (C-26), 62.4, 62.1, 61.2 (C-6″), 55.9, 53.6, 48.3, 41.6, 40.5, 39.8, 37.6 (*C*H$_2$ of Lev), 37.4, 36.7, 33.5, 31.6, 31.3, 30.3, 29.6 (*C*H$_3$ of Lev), 29.1, 28.9, 28.7, 27.5 (*C*H$_2$ of Lev), 21.2 (*C*H$_3$ of Ac), 20.8, 17.1 (C-27), 16.4 (C-18), 14.4 (C-21), 13.3 (C-19); HRMS (ESI) calcd for $C_{88}H_{100}O_{21}Na$ $[M+Na]^+$: 1515.6649, found: 1515.6642.

4.3.21. Chlorogenin 3β-*O*-{2-*O*-[2,3,6-tri-*O*-benzoyl-4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-glucopyranosyl]-3,6-di-*O*-benzyl-4-*O*-levulinoyl-β-D-glucopyranoside} 6α-acetate (37)

According to the general procedure for glycosylation, treatment of **28** (90 mg, 0.10 mmol) and **22** (179 mg, 0.15 mmol) in CH_2Cl_2 afforded **37** (93 mg, 48%) as a white solid: mp 129 °C; $[\alpha]_D^{25}$ +3.0 (*c* 0.07, CH_2Cl_2); ^1H NMR ($CDCl_3$, 600 MHz) δ 8.02 (d, *J* = 7.9 Hz, 2H, H-Ar), 7.95–7.88 (m, 7H, H-Ar), 7.85 (d, *J* = 7.9 Hz, 2H, H-Ar), 7.77 (d, *J* = 7.9 Hz, 2H, H-Ar), 7.68 (d, *J* = 8.0 Hz, 2H, H-Ar), 7.76 (t, *J* = 7.6 Hz, 1H, H-Ar), 7.54–7.53 (m, 2H, H-Ar), 7.47–7.36 (m, 8H, H-Ar), 7.32–7.16 (m, 15H, H-Ar), 7.12 (t, *J* = 7.7 Hz, 2H, H-Ar), 6.98 (d, *J* = 7.1 Hz, 2H, H-Ar), 5.72–5.63 (m, 3H, H-3″, H-4‴, H-2‴), 5.44 (t, *J* = 8.1 Hz, 1H, H-2″), 5.27 (m, 1H, H-3‴), 5.18 (d, *J* = 8.0 Hz, 1H, H-1″), 4.87 (d, *J* = 8.0 Hz, 1H, H-1‴), 4.76 (t, *J* = 9.0 Hz, 1H, H-4′), 4.59–4.56 (m, 3H, H-6a″, H-6, C*H*$_2$ of Bn), 4.50 (d, *J* = 7.4 Hz, 1H, H-1′), 4.45–4.44 (m, 1H, C*H*$_2$ of Bn), 4.43–4.42 (m, 3H, H-6b″, C*H*$_2$ of Bn), 4.39–4.36 (m, 1H, H-16), 4.34 (t, *J* = 9.5 Hz, 1H, H-4″), 4.27 (d, *J* = 12.1 Hz, 1H, C*H*$_2$ of Bn), 3.80–3.79 (m, 1H, H-5‴), 3.73–3.71 (m, 2H, H-5″, H-6a‴), 3.64–3.60 (m, 2H, H-2′, H-6b‴), 3.55–3.54 (m, 1H, H-3), 3.51–3.35 (m, 5H, H-3′, H-6a′, H-6b′, H-26, H-5′), 2.43–2.29 (m, 2H, C*H*$_2$ of Lev), 2.17–2.15 (m, 2H, C*H*$_2$ of Lev), 2.06 (s, 3H, C*H*$_3$ of Lev), 2.00 (s, 3H, CH_3 of Ac), 1.90–1.88 (m, 5H), 1.80–1.53 (m, 8H), 1.51–1.03 (m, 9H), 0.85–0.82 (m, 2H), 0.96 (d, *J* = 6.9 Hz, 3H, H-21), 0.78 (d, *J* = 6.3 Hz, 3H, H-27), 0.75 (s, 3H, H-19), 0.72–0.70 (m, 1H), 0.57 (s, 3H, H-18), 0.55–0.52 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 206.1 (C=O), 171.5, 170.8, 165.7, 165.5, 165.36, 165.35, 165.30, 165.2, 164.8 (OC=O), 138.4, 138.1, 133.4–133.0, 129.9–127.1, 109.2 (C-22), 101.0 (C-1‴), 100.1 (C-1″), 99.9 (C-1′), 82.3 (C-3′), 80.7 (C-2′), 80.6 (C-16), 78.2 (C-3), 75.8 (C-4″), 75.1 (*C*H$_2$ of Bn), 73.3 (*C*H$_2$ of Bn), 73.18 (C-3″), 73.05 (C-5′), 73.04 (C-5″), 72.6 (C-2″), 72.1 (C-6), 71.9 (C-3‴), 71.28 (C-4′), 71.26 (C-5‴), 69.8 (C-2‴), 69.7 (C-6′), 67.4 (C-4‴), 66.9 (C-26), 62.4 (C-6″), 62.1, 60.7 (C-6‴), 55.8, 53.4, 48.4, 41.6, 40.5, 39.7, 37.7, 37.5 (*C*H$_2$ of Lev), 36.8, 36.5, 33.6, 31.7, 31.3, 30.3, 29.6 (CH_3 of Ac), 29.0, 28.9, 28.7, 27.6 (*C*H$_2$ of Lev), 21.4 (*C*H$_3$ of Lev), 20.8, 17.1 (C-27), 16.4 (C-19), 14.4 (C-21), 13.0 (C-18); HRMS (ESI) calcd for $C_{115}H_{122}O_{29}Na$ $[M+Na]^+$: 1990.7998, found: 1990.7787.

4.3.22. Chlorogenyl 3β-*O*-[2-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-3,6-di-*O*-benzyl-4-*O*-levulinoyl-β-D-glucopyranoside] 6α-acetate (38)

According to the general procedure for glycosylation, treatment of **28** (2.00 g, 2.19 mmol) and **23** (2.04 g, 3.28 mmol) in CH_2Cl_2 afforded **38** (1.46 g, 49%) as a white solid: mp, 125 °C; $[\alpha]_D^{25}$ +145.0 (*c* 0.12, CH_2Cl_2); ^1H NMR ($CDCl_3$, 600 MHz) δ 7.98 (d, *J* = 7.9 Hz, 2H, H-Ar), 7.92 (d, *J* = 7.5 Hz, 2H, H-Ar), 7.80 (d, *J* = 8.0 Hz, 2H, H-Ar), 7.56 (t, *J* = 7.4 Hz, 1H, H-Ar), 7.50 (t, *J* = 7.4 Hz, 1H, H-Ar), 7.45–7.21 (m, 14H, H-Ar), 7.12 (t, *J* = 7.5 Hz, 2H, H-Ar), 7.04 (t, *J* = 7.5 Hz, 1H, H-Ar), 5.75 (m, 2H, H-2″, H-3″), 5.60 (t, *J* = 9.8 Hz, 1H, H-4″), 5.38 (s, 1H,H-1″), 4.99 (t, *J* = 9.4 Hz, 1H, H-4′), 4.82 (d, 1H, *J* = 11.2 Hz, C*H*$_2$ of Bn), 4.72–4.66 (m, 3H, H-6, H-5″, C*H*$_2$ of Bn), 4.63 (d, *J* = 7.6 Hz, 1H, H-1′), 4.54 (s, 2H, C*H*$_2$ of Bn), 4.38 (dd, *J* = 7.4, 15.0 Hz, 1H, H-16), 3.83 (t, *J* = 9.1 Hz, 1H, H-3′), 3.80–3.72 (m, 2H, H-2′, H-3), 3.60 (m, 2H, H-5′, H-6a′), 3.55 (m, 1H, H-6b′), 3.44–3.43 (m, 1H, H-26a), 3.36 (t, *J* = 11.0 Hz, 1H, H-26b), 2.60–2.50 (m, 2H, C*H*$_2$ of Lev), 2.40–2.20 (m, 2H, C*H*$_2$ of Lev), 2.15–2.14 (m, 1H), 2.10 (s, 3H, C*H*$_3$ of Lev), 2.07–2.06 (m, 1H), 2.03 (s, 3H, C*H*$_3$ of Ac), 1.94–1.84 (m, 4H), 1.76–1.43 (m, 12H), 1.30 (d, *J* = 6.2 Hz, 3H, CH_3-6″), 1.29–1.09 (m, 6H), 0.95 (d, *J* = 7.0 Hz, 3H, H-21), 0.87–0.86 (m, 1H), 0.78 (d, *J* = 6.3 Hz, 3H, H-27), 0.72 (s, 3H, H-19), 0.69 (s, 3H, H-18), 0.67–0.66 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 206.0 (C=O), 171.6, 170.7, 165.9, 165.5, 165.2 (OC=O), 138.1, 137.7, 133.2, 133.2, 132.9, 129.8, 129.6, 129.6, 129.4, 129.3, 129.2, 128.4–128.1, 127.7–127.4, 109.1 (C-22), 98.4 (C-1′), 97.6 (C-1″), 83.7 (C-3′), 80.5 (C-16), 76.7 (C-3), 76.3 (C-2′), 75.3 (*C*H$_2$ of Bn), 73.4 (*C*H$_2$ of Bn), 72.3 (C-6), 71.77 (C-4′), 71.77 (C-4″), 70.5 (C-2″), 70.0 (C-3″), 69.7 (C-6′), 66.8 (C-26), 66.7 (C-5″), 62.0, 55.8, 53.6, 48.2, 41.5, 40.5, 39.7, 37.7, 37.6 (*C*H$_2$ of Lev), 37.1, 36.6, 33.6, 31.6, 31.3, 30.2, 29.6 (CH_3 of Lev), 29.0, 28.7, 27.9, 27.7 (*C*H$_2$ of Lev), 21.2 (*C*H$_3$ of Ac), 20.7, 17.4 (C-6″), 17.0 (C-27), 16.3 (C-19), 14.4 (C-21), 13.0 (C-18); HRMS (ESI) calcd for $C_{81}H_{96}O_{19}Na$ $[M+Na]^+$: 1395.6438, found: 1395.6329.

4.3.23. Chlorogenin 3β-*O*-{2-*O*-[2,3-di-*O*-isopropylidene-4-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-α-L-rhamnopyranosyl]-3,6-di-*O*-benzyl-4-*O*-levulinyl-β-D-glucopyranoside} 6α-acetate (39)

According to the general procedure for glycosylation, treatment of **28** (90 mg, 0.10 mmol) and **24** (119 mg, 0.15 mmol) in CH_2Cl_2 afforded **39** (73 mg, 48%) as a white solid: mp 136 °C; $[\alpha]_D^{25}$ +19.9 (*c* 0.01, CH_2Cl_2); ^1H NMR ($CDCl_3$, 600 MHz) δ 8.10 (d, *J* = 7.1 Hz, 2H, H-Ar), 7.93 (d, *J* = 7.2H, H-Ar), 7.76 (d, *J* = 7.2 Hz, 2H, H-Ar), 7.60–7.19 (m, 19H, H-Ar), 5.75 (m, 1H, H-3‴), 5.71 (m, 1H, H-2‴), 5.63 (t, *J* = 9.8 Hz, 1H, H-4‴), 5.56 (d, *J* = 1.4 Hz, 1H, H-1‴), 5.38 (s, 1H, H-1″), 4.98 (m, 1H, H-4′), 4.75 (m, 1H, H-6), 4.67 (dd, *J* = 11.2, 14.6 Hz, 2H, C*H*$_2$ of Bn), 4.51 (m, 3H, C*H*$_2$ of Bn, H-1′), 4.33 (dd, *J* = 7.3, 15.6 Hz, 1H, H-16), 4.21–4.12 (m, 3H, H-3″, H-5″, H-5‴), 4.07 (d, *J* = 5.6 Hz, 1H, H-2″), 3.69 (m, 3H, H-2′, H-3′, H-3), 3.59–3.53 (m, 4H, H-4″, H-5′, H-6a′, H-6b′), 3.44 (m, 1H, H-26a), 3.34 (t, *J* = 11.1 Hz, 1H, H-26b), 2.64–2.52 (m, 2H, C*H*$_2$ of Lev), 2.40–2.29 (m, 2H, C*H*$_2$ of Lev), 2.11 (s, 3H, C*H*$_3$ of Ac), 2.06 (s, 3H, C*H*$_3$ of Lev), 1.97–1.88 (m, 4H), 1.79–1.51 (m, 14H), 1.49 (s, 3H, CC*H*$_3$), 1.36 (d, *J* = 6.3 Hz, 3H, H-6″), 1.33 (d, *J* = 6.3 Hz, 3H, H-6‴),

1.27 (s, 3H, $C(CH_3)_2$), 1.21 (m, 3H), 1.09–1.00 (m, 3H), 0.94 (s, 3H, H-19), 0.92 (d, J = 7.0 Hz, 3H, H-21), 0.88–0.87 (m, 1H), 0.77 (d, J = 6.2 Hz, 3H, H-27), 0.67–0.65 (m, 1H), 0.59 (s, 3H, H-18); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 206.1 (C=O), 171.7, 170.4, 165.7, 165.3, 165.2 (OC=O), 138.1, 137.6, 133.2, 133.2, 132.9, 129.9–127.6, 109.4 ($C(CH_3)_2$), 109.2 (C-22), 98.9 (C-1′), 97.5 (C-1″), 95.9 (C-1‴), 82.9 (C-3′), 80.6 (C-16), 77.9 (C-3″), 77.2 (C-6′), 77.0 (C-3), 76.5 (C-2′), 76.0 (C-2″), 75.0 (CH_2 of Bn), 73.5 (CH_2 of Bn), 73.4 (C-5′), 72.4 (C-6), 71.96 (C-4′), 71.90 (C-4‴), 70.9 (C-2‴), 69.9 (C-6′), 69.8 (C-3‴), 67.2 (C-5‴), 66.8 (C-26), 64.3 (C-5″), 62.0, 55.9, 53.7, 48.4, 41.5, 40.5, 39.8, 37.8, 37.6 (CH_2 of Lev), 37.0, 36.8, 33.5, 31.6, 31.3, 30.3, 29.7 (CH_3 of Ac), 28.8, 28.7, 27.8 (CH_2 of Lev), 26.3, 21.3 (CH_3 of Lev), 20.9, 18.1 (C-6″), 17.6 (C-6‴), 17.0 (C-27), 16.2 (C-18), 14.4 (C-21), 13.2 (C-19); HRMS (ESI) calcd for $C_{90}H_{110}O_{23}Na$ [M+Na]$^+$: 1581.7330, found: 1581.7284.

4.3.24. Chlorogenin 3β-*O*-[4-*O*-(2,3,4-tri-*O*-benzoyl-β-L-arabinopyranosyl)-3,6-di-*O*-benzyl-2-*O*-(2-nitro)phenylacetyl-β-D-glucopyranoside] 6α-acetate (40)

According to the general procedure for glycosylation, treatment of **29** (90 mg, 0.09 mmol) and **15** (83 mg, 0.14 mmol) in CH_2Cl_2 afforded **40** (115 mg, 89%) as a white solid: mp 145 °C; $[\alpha]_D^{25}$ +11.9 (c 0.03, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.01 (d, J = 7.3 Hz, 2H, H-Ar), 7.91 (d, J = 8.3 Hz, 2H, H-Ar), 7.82 (d, J = 7.4 Hz, 2H, H-Ar), 7.56–7.03 (m, 23H, H-Ar), 5.71 (t, J = 8.2 Hz, 1H, H-2″), 5.53 (s, 1H, H-4″), 5.36 (d, J = 10.0 Hz, 1H, H-3″), 4.97 (t, J = 8.8 Hz, 1H, H-2′), 4.95 (d, J = 9.9 Hz, 1H, CH_2 of Bn), 4.77 (d, J = 7.6 Hz, 1H, H-1″), 4.71 (d, J = 10.0 Hz, 1H, CH_2 of Bn), 4.61–4.60 (m, 1H, H-6), 4.58 (d, J = 12.1 Hz, 1H, CH_2 of Bn), 4.49 (d, J = 7.7 Hz, 1H, H-1′), 4.34 (m, 1H, H-16), 4.32 (d, J = 12.2 Hz, 1H, CH_2 of Bn), 4.10 (t, J = 9.1 Hz, 1H, H-4′), 3.95 (d, J = 12.8 Hz, 1H, H-5a″), 3.75 (t, J = 8.8 Hz, 1H, H-3′), 3.60 (d, J = 10.7 Hz, 1H, H-6a′), 3.52 (d, J = 10.7 Hz, 1H, H-6b′), 3.46–3.44 (m, 4H, H-3, H-5b″, CH_2 of NPAc), 3.34–3.32 (m, 2H, H-26a, H-26b), 3.26 (d, J = 10.9 Hz, 1H, H-5′), 1.96 (s, 3H, CH_3 of Ac), 1.90–1.57 (m, 12H), 1.33–1.02 (m, 10H), 0.86 (m, 3H), 0.93 (d, J = 6.8 Hz, 3H, H_3-21), 0.83 (s, 3H, H-19), 0.77 (d, J = 5.9 Hz, 3H, H-27), 0.73 (s, 3H, H-18), 0.62–0.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 170.1, 165.6, 165.6, 165.0, 162.8 (OC=O), 146.7, 138.1, 138.0, 133.4, 133.4, 133.1, 129.7–127.5, 109.3 (C-22), 100.9 (C-1″), 98.6 (C-1′), 80.7 (C-16), 80.4 (C-3′), 78.0 (C-3), 77.0 (C-4′), 76.8 (C-2′), 74.5 (C-5′), 74.4, 73.4 (CH_2 of Bn), 72.3 (C-6), 71.3 (C-3″), 70.5 (C-2″), 69.0 (C-4″), 67.7 (C-6′), 66.9 (C-26), 63.8 (C-5″), 62.1, 55.9, 53.7, 48.4, 41.5, 40.5, 39.8 (CH_2 of NPAc), 37.8, 37.1, 36.7, 33.6, 31.6, 31.3, 30.3, 29.6, 28.8, 28.7, 27.9, 21.2 (CH_3 of Ac), 20.8, 17.1 (C-27), 16.3 (C-18), 14.4 (C-21), 13.2 (C-19); HRMS (ESI) calcd for $C_{83}H_{93}NO_{20}Na$ [M+Na]$^+$: 1446.6183, found: 1446.6182.

4.3.25. Chlorogenin 3β-*O*-[4-*O*-(2,3,4-tri-*O*-benzoyl-β-L-fucopyranosyl)-3,6-di-*O*-benzyl-2-*O*-(2-nitro)phenylacetyl-β-D-glucopyranoside] 6α-acetate (41)

According to the general procedure for glycosylation, treatment of **29** (90 mg, 0.09 mmol) and **16** (86 mg, 0.14 mmol) in CH_2Cl_2 afforded **41** (60 mg, 45%) as a white solid: mp 124 °C; $[\alpha]_D^{25}$ −49.9 (c 0.05, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.07 (d, J = 7.2 Hz, 2H, H-Ar), 7.86 (d, J = 7.3 Hz, 2H, H-Ar), 7.72 (d, J = 7.3 Hz, 2H, H-Ar), 7.47–7.09 (m, 23H, H-Ar), 5.70 (dd, J = 10.4, 7.8 Hz, 1H, H-2″), 5.62 (d, J = 3.5 Hz, 1H, H-4″), 5.45 (dd, J = 10.4, 3.5 Hz, 1H, H-3″), 5.14 (d, J = 7.7 Hz, 1H, H-1″), 4.88 (dd, J = 9.4, 9.4 Hz, 1H, H-2′), 4.65–4.64 (m, 1H, H-6), 4.61 (br s, 2H, CH_2 of Bn), 4.54 (d, 1H, J = 11.7 Hz, CH_2 of Bn), 4.39 (d, J = 7.7 Hz, 1H, H-1′), 4.36 (dd, J = 7.2, 15.4 Hz, 1H, H-16), 4.23 (d, J = 11.2 Hz, 1H, CH_2 of Bn), 4.10–4.09 (m, 2H, H-6a′, H-6b′), 3.89 (q, J = 6.1 Hz, 1H, H-5″), 3.85 (d, J = 9.4 Hz, 1H, H-4′), 3.74 (s, 2H, CH_2 of NPAC), 3.57–3.56 (m, 1H, H-5′), 3.52 (t, J = 9.2 Hz, 1H, H-3′), 3.46–3.43 (m, 2H, H-3, H-26a), 3.35 (t, J = 10.9 Hz, 1H, H-26b), 1.99 (s, 3H, CH_3 of Ac), 1.98–1.83 (m, 6H), 1.74 (m, 1H), 1.71–1.27 (m, 15H), 1.11–1.09 (m, 3H), 1.20 (d, J = 6.4 Hz, 3H, H-6″), 0.94 (d, J = 7.0 Hz, 3H, H-21), 0.88 (m, 2H), 0.82 (s, 3H, H-19), 0.77 (d, J = 6.3 Hz, 3H, H-27), 0.73 (s, 3H, H-18), 0.64 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 171.1, 168.1, 165.8, 165.5, 165.3 (OC=O), 149.1, 138.6, 133.4, 133.2, 133.1, 132.8, 129.9–127.1, 109.2 (C-22), 100.2 (C-1″), 98.5 (C-1′), 83.1 (C-3′), 80.6 (C-16), 77.6 (C-3), 74.8 (C-4′), 74.7 (CH_2 of Bn), 74.49 (C-5′), 74.40 (C-2′), 73.6 (CH_2 of Bn), 72.3 (C-6), 72.0 (C-3″), 71.1 (C-4″), 70.3 (C-2″), 69.5 (C-5″), 66.8 (C-26), 62.1, 60.3 (C-6′), 55.9, 53.7, 48.3, 41.6, 40.5, 39.8, 39.0 (CH_2 of NPAc), 37.8, 37.0, 36.7, 33.6, 31.6, 31.3, 30.3, 28.8, 28.7, 28.2, 22.6, 21.3 (CH_3 of Ac), 20.8, 17.11 (C-27), 16.4 (C-18), 16.0 (C-6″), 14.4 (C-21), 13.2 (C-19); HRMS (ESI) calcd for $C_{84}H_{95}NO_{20}Na$ [M+Na]$^+$: 1460.6340, found: 1460.6220.

4.3.26. Chlorogenin 3β-*O*-[4-*O*-(2,3,4-tri-*O*-benzoyl-β-L-xylopyranosyl)-3,6-di-*O*-benzyl-2-*O*-(2-nitro)phenylacetyl-β-D-glucopyranoside] 6α-acetate (42)

According to the general procedure for glycosylation, treatment of **29** (90 mg, 0.09 mmol) and **17** (84 mg, 0.14 mmol) in CH_2Cl_2 afforded **42** (72 mg, 55%) as a white solid: mp 111 °C; $[\alpha]_D^{25}$ −3.1 (c 0.03, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.82–7.92 (m, 8H, H-Ar), 7.55–7.38 (m, 4H, H-Ar), 7.39–7.25 (m, 15H, H-Ar), 7.09 (m, 2H, H-Ar), 5.70 (t, J = 8.8 Hz, 1H, H-3″), 5.38 (dd, J = 7.1, 9.2 Hz, 1H, H-2″), 5.26–5.24 (m, 1H, H-4″), 5.15–5.13 (m, 1H, H-1″), 4.88 (dd, J = 7.6, 9.4 Hz, 1H, H-2′), 4.65 (m, 1H, H-6), 4.61 (m, 2H, CH_2 of Bn), 4.50 (d, J = 11.5 Hz, 1H, CH_2 of Bn), 4.36 (m, 2H, H-1′, H-16), 4.22 (m, 2H, CH_2 of Bn, H-5a″), 3.95 (d, J = 9.8 Hz, 1H, H-6a′), 4.80 (t, J = 9.2 Hz, 1H, H-4′), 3.75 (d, J = 2.3 Hz, 2H, CH_2 of NPAc), 3.61 (m, 1H, H-6b′), 3.53 (m, 2H, H-5′, H-3′), 3.44 (m, 3H, H-3, H-26a, H-5b″), 3.35 (m, 1H, H-26b), 2.02 (s, 3H, CH_3 of Ac), 2.01–1.91(m, 3H), 1.84–1.75 (m, 4H), 1.71–1.40 (m, 12H), 1.23–1.12 (m, 4H), 0.94 (d, J = 7.0 Hz, 3H, H-21), 0.88 (m, 2H), 0.82 (s, 3H, H-19), 0.77 (d, J = 6.3 Hz, 3H, H-27), 0.73 (s, 3H, H-18), 0.64 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 170.9, 168.1, 165.5, 165.5, 165.1 (OC=O), 133.4, 133.2, 133.1, 132.8, 129.8, 129.7, 129.0–127.1, 125.0, 109.2 (C-22), 100.4 (C-1″), 98.5 (C-1′), 83.3 (C-3′), 80.6 (C-16), 77.6 (C-3), 74.6 (C-4′), 74.6 (CH_2 of Bn), 74.38 (C-5′), 74.38 (C-2′), 73.34 (CH_2 of Bn), 72.3 (C-6), 71.6 (C-3″), 71.5 (C-2″), 69.7 (C-4″), 69.5 (C-6′), 66.8 (C-26), 62.2 (C-5″), 62.1, 55.9, 53.7, 48.4, 48.3, 45.6, 40.5, 39.8, 39.0 (CH_2 of NPAc), 37.8, 37.0, 36.7, 33.6, 31.6, 31.3, 30.3, 28.8, 28.7, 21.3 (CH_3-Ac), 20.8, 17.1 (C-27), 16.3 (C-18), 14.4 (C-21), 13.2 (C-19); HRMS (ESI) calcd for $C_{83}H_{93}NO_{20}Na$ [M+Na]$^+$: 1446.6183, found: 1446.6070.

4.3.27. Chlorogenin 3β-*O*-[4-*O*-(2,3,4-tri-*O*-benzoyl-β-D-xylopyranosyl)-3,6-di-*O*-benzyl-2-*O*-(2-nitro)phenylacetyl-β-D-glucopyranoside] 6α-acetate (43)

According to the general procedure for glycosylation, treatment of **29** (90 mg, 0.09 mmol) and **18** (84 mg, 0.14 mmol) in CH_2Cl_2 afforded **43** (74 mg, 57%) as a white solid: mp 116–120 °C; $[\alpha]_D^{25}$ −18.6 (c 0.07, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.97–7.85 (m, 6H, H-Ar), 7.54–7.18 (m, 23H, H-Ar), 5.65 (d, J = 6.5 Hz, 1H, H-3″), 5.37–5.34 (m, 1H, H-2″), 5.24–5.22 (m, 1H, H-4″), 4.88 (dd, J = 6.6, 9.5 Hz, 1H, H-2′), 4.83 (d, 1H, J = 10.8 Hz, 1H, CH_2 of Bn), 4.81 (d, J = 6.7 Hz, 1H, H-1″), 4.62–4.60 (m, 1H, H-6), 4.56 (d, J = 11.3 Hz, 1H, CH_2 of Bn), 4.44 (d, J = 11.3 Hz, 1H, CH_2 of Bn), 4.36–4.33 (m, 3H, H-16, CH_2 of Bn, H-1′), 4.17 (dd, J = 11.7, 4.9 Hz, 1H, H-5a″), 3.98 (t, J = 9.3 Hz, 1H, H-4′), 3.91 (d, J = 11.7 Hz, 2H, CH_2 of NPAC), 3.60 (dd, J = 10.8, 3.4 Hz, 1H, H-6a′), 3.55 (t, J = 8.8 Hz, 1H, H-3′), 3.50 (d, J = 11.1 Hz, 1H, H-6b′), 3.44–3.41 (m, 1H, H-26a), 3.39–3.37 (m, 1H, H-3), 3.35 (t, J = 10.8 Hz, 1H, H-26b), 3.24–3.22 (m, 2H, H-5b″, H-5′), 1.97 (s, 3H, CH_3 of Ac), 1.90–1.82 (m, 3H), 1.76–1.54 (12H), 1.44–1.23 (m, 4H), 1.10–1.08 (m, 4H), 0.93 (d, J = 7.1 Hz, 3H, H-21), 0.87–0.86 (m, 2H), 0.81 (s, 3H, H-19), 0.77 (d, J = 6.4 Hz, 3H, H-27),

0.73 (s, 3H, H-18), 0.62–0.61(m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 170.8, 167.9, 165.5, 165.4, 164.9 (OC=O), 149.3, 146.6, 138.4, 138.1, 138.0, 137.9, 133.3–127.5, 109.2 (C-22), 100.7 (C-1″), 98.8 (C-1′), 81.0 (C-3′), 80.6 (C-16), 77.8 (C-3), 76.9 (C-4′), 74.7 (*C*H$_2$ of Bn), 74.6 (C-5′), 73.8 (C-2′), 73.3 (*C*H$_2$ of Bn), 72.3 (C-6), 71.9 (C-3″), 71.7 (C-2″), 69.7 (C-4″), 67.7 (C-6′), 66.8 (C-26), 62.3, 62.1 (C-5″), 55.9, 53.7, 48.3, 41.5, 40.5, 39.8, 39.1 (*C*H$_2$ of NPAc), 37.8, 37.0, 36.7, 33.6, 31.6, 31.3, 30.8, 30.2, 28.8, 28.7, 21.3 (*C*H$_3$-Ac), 20.8, 17.0 (C-27), 16.3 (C-18), 14.4 (C-21), 13.2 (C-19); HRMS (ESI) calcd for $C_{83}H_{93}NO_{20}Na$ [M+Na]$^+$: 1446.6183, found: 1446.6223.

4.3.28. Chlorogenin 3β-*O*-[4-*O*-(2,3,4-tri-*O*-benzoyl-α-D-mannopyranosyl)-3,6-di-*O*-benzyl-2-*O*-(2-nitro)phenylacetyl-β-D-glucopyranoside] 6α-acetate (44)

According to the general procedure for glycosylation, treatment of **29** (90 mg, 0.09 mmol) and **19** (102 mg, 0.14 mmol) in CH_2Cl_2 afforded **44** (100 mg, 70%) as a white solid: mp 107–110 °C; $[\alpha]_D^{25}$ −29.1 (*c* 0.06, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.06–7.01 (m, 34H, H-Ar), 6.14 (t, *J* = 10.2 Hz, 1H, H-4″), 5.99–5.98 (m, 1H, H-3″), 5.57–5.56 (m, 1H, H-2″), 5.50 (br s, 1H, H-1″), 4.99 (t, *J* = 8.4 Hz, 1H, H-2′), 4.69 (m, 1H, H-6), 4.63–4.62 (m, 3H, H-5″, C*H*$_2$ of Bn), 4.60–4.53 (m, 2H, C*H*$_2$ of Bn), 4.50 (d, *J* = 7.8 Hz, 1H, H-1′), 4.44 (m, 1H, H-6a″), 4.37–4.36 (m, 1H, H-16), 4.24–4.20 (m, 1H, H-6b″), 3.96–3.89 (m, 3H, H-4′, C*H*$_2$ of NPAc), 3.85–3.78 (m, 3H, H-6a′, H-6b′, H-3′), 3.64–3.61 (m, 1H, H-5′), 3.54–3.50 (m, 1H, H-3), 3.46–3.44 (m, 1H, H-26a), 3.36–3.31 (m, 1H, H-26b), 2.02 (s, 3H, C*H*$_3$ of Ac), 1.93–1.84 (m, 3H), 1.78–1.41 (m, 15H), 1.27 (m, 3H), 1.21–1.10 (m, 2H), 0.95 (d, *J* = 7.0 Hz, 3H, H-21), 0.89–0.88 (m, 2H), 0.86 (s, 3H, H-19), 0.77 (d, *J* = 6.3 Hz, 3H, H-27), 0.75 (s, 3H, H-18), 0.68–0.66 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 171.1, 170.9, 170.7, 166.0, 165.6, 165.2 (OC=O), 149.2, 146.5, 138.0, 137.5, 137.0, 133.4–132.9, 130.0–127.2, 125.1, 109.2 (C-22), 98.8 (C-1′), 97.8 (C-1″), 82.9 (C-3′), 80.6 (C-16), 74.9 (C-4′), 74.5 (C-5′), 74.4 (C-2′), 73.5, 73.5 (*C*H$_2$ of Bn), 72.3 (C-6), 70.2 (C-2″), 69.3 (C-6′), 68.9 (C-5″), 66.87 (C-26), 66.87 (C-4″), 66.5 (C-3″), 62.6 (C-6″), 62.1, 60.3, 55.9, 53.7, 53.4, 41.6, 40.5, 39.8, 39.2 (*C*H$_2$ of NPAc), 37.8, 37.1, 36.7, 33.6, 31.6, 31.3, 30.3, 29.6, 28.7, 21.3 (CH$_3$ of Ac), 20.9, 17.1 (C-27), 16.4 (C-18), 14.4 (C-21), 13.3 (C-19); HRMS (ESI) calcd for $C_{91}H_{99}NO_{22}Na$ [M+Na]$^+$: 1581.6585, found: 1581.6509.

4.3.29. Chlorogenin 3β-*O*-[4-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl)-3,6-di-*O*-benzyl-2-*O*-(2-nitro)phenylacetyl-β-D-glucopyranoside] 6α-acetate (45)

According to the general procedure for glycosylation, treatment of **29** (90 mg, 0.09 mmol) and **20** (102 mg, 0.14 mmol) in CH_2Cl_2 afforded **45** (92 mg, 62%) as a white solid: mp 102 °C; $[\alpha]_D^{25}$ −17.5 (*c* 0.04, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.92–7.77 (m, 6H, H-Ar), 7.48–7.47 (m, 23H, H-Ar), 7.19–7.16 (m, 5H, H-Ar), 5.68 (t, *J* = 9.6 Hz, 1H, H-2″), 5.50 (t, *J* = 9.6 Hz, 1H, H-3″), 5.46 (t, *J* = 9.6 Hz, 1H, H-4″), 4.93 (d, *J* = 12.0 Hz, 1H, C*H*$_2$ of Bn), 4.88–4.86 (m, 2H, H-1″, C*H*$_2$ of Bn), 4.64–4.62 (m, 2H, H-6, C*H*$_2$ of Bn), 4.42–4.40 (m, 2H, C*H*$_2$ of Bn, H-1′), 4.35–4.30 (m, 3H, H-6a′, H-6b′, H-16), 4.09 (dd, *J* = 6.0, 12.0 Hz, 1H, H-6a″), 4.01 (t, *J* = 12.0 Hz, 1H, H-6b″), 3.80 (br s, 2H, C*H*$_2$ of NPAc), 3.75–3.74 (m, 1H, H-26a), 3.61–3.59 (m, 1H, H-26b), 3.55 (t, *J* = 9.1 Hz, 1H, H-3′), 3.45–3.33 (m, 3H, H-5′, H-3, H-5″), 3.21 (br d, *J* = 10.9 Hz, 1H, H-2′), 2.00 (s, 3H, C*H*$_3$-Ac), 1.98–1.95 (m, 1H), 1.84–1.41 (m, 16H), 1.26–1.06 (m, 7H), 0.94 (d, *J* = 6.9 Hz, 3H, H-21), 0.87 (m, 1H), 0.84 (s, 3H, H-19), 0.77 (d, *J* = 6.3 Hz, 3H, H-27), 0.76 (s, 3H, H-18), 0.66 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 170.9, 168.1, 166.0, 165.7, 165.1, 164.9, 135.8, 133.4, 133.4, 133.2, 133.1, 133.1, 132.8, 130.0, 129.9, 129.8, 129.7, 129.7, 129.5, 129.0, 128.8, 128.6, 128.6, 128.5, 128.4, 128.4, 128.3, 128.2, 128.1, 128.0, 127.2, 125.0, 109.3 (C-22), 100.6 (C-1″), 98.8 (C-1′), 80.8, 80.7, 79.2, 77.9, 77.5, 74.5, 74.4, 73.6, 73.4, 73.0, 72.3, 72.2, 72.0, 69.7, 67.6, 66.9, 62.8, 62.1, 56.0, 53.7, 48.4, 41.6, 40.6, 39.8, 39.0 (*C*H$_2$ of NPAc), 37.8, 37.1, 36.7, 33.6, 31.6, 31.3, 30.3, 28.8, 28.7, 28.2, 21.3, 20.9 (*C*H$_3$ of Ac), 17.1 (C-27), 16.4 (C-18), 14.5 (C-21), 13.3 (C-19); HRMS (ESI) calcd for $C_{91}H_{99}NO_{22}Na$ [M+Na]$^+$: 1581.6585, found: 1581.6576.

4.3.30. Chlorogenin 3β-*O*-[4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-3,6-di-*O*-benzyl-2-*O*-(2-(nitro)phenylacetyl-β-D-glucopyranoside] 6α-acetate (46)

According to the general procedure for glycosylation, treatment of **29** (90 mg, 0.09 mmol) and **21** (102 mg, 0.14 mmol) in CH_2Cl_2 afforded **46** (49 mg, 34%) as a white solid: mp 110 °C; $[\alpha]_D^{25}$ +3.1 (*c* 0.03, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.95 (t, *J* = 9.1 Hz, 4H, H-Ar), 7.87 (d, *J* = 7.3 Hz, 2H, H-Ar), 7.74 (t, *J* = 8.2 Hz, 2H, H-Ar), 7.57–7.12 (m, 26H, H-Ar), 5.80 (d, *J* = 3.5 Hz, 1H, H-4″), 5.70 (dd, *J* = 7.9, 10.6 Hz, 1H, H-2″), 5.37 (dd, *J* = 3.7, 10.6 Hz, 1H, H-3″), 5.01 (d, *J* = 11.1 Hz, 1H, C*H*$_2$ of Bn), 4.91 (dd, *J* = 9.0, 7.9 Hz, 1H, H-2′), 4.88 (d, *J* = 7.9 Hz, 1H, H-1″), 4.64–4.61 (m, 1H, H-6), 4.62 (d, *J* = 12.1 Hz, 1H, C*H*$_2$ of Bn), 4.51 (d, *J* = 11.6 Hz, 1H, C*H*$_2$ of Bn), 4.37–4.30 (m, 3H, H-16, C*H*$_2$ of Bn, H-1′), 4.19–4.16 (m, 2H, H-6a″, H-6b″), 4.06 (t, *J* = 9.0 Hz, 1H, H-4′), 3.95–3.87 (m, 3H, H-5″, C*H*$_2$ of NPAC), 3.61 (dd, *J* = 11.1, 3.7 Hz, 1H, H-6a′), 3.59 (t, *J* = 9.5 Hz, 1H, H-3′), 3.51 (d, *J* = 10.0 Hz, 1H, H-6b′), 3.44–3.40 (m, 1H, H-26a), 3.38–3.36 (m, 1H, H-3), 3.35 (t, *J* = 11.1 Hz, 1H, H-26b), 3.24–3.15 (m, 1H, H-5′), 2.01 (s, 3H, C*H*$_3$ of Ac), 2.00–1.39 (m, 18H), 1.29–1.05 (m, 5H), 0.93 (d, *J* = 6.9 Hz, 3H, H-21), 0.86–0.84 (m, 2H), 0.82 (s, 3H, H-19), 0.77 (d, *J* = 6.3 Hz, 3H, H-27), 0.73 (s, 3H, H-18), 0.63–0.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 170.8, 167.9, 165.9, 165.4, 165.3, 165.0 (OC=O), 149.3, 138.8, 138.0, 133.4, 133.4, 133.2, 133.0, 129.9–125.0, 109.2 (C-22), 100.5 (C-1″), 98.9 (C-1′), 80.65 (C-16), 80.60 (C-3′), 77.8 (C-3), 76.9 (C-4′), 74.5 (C-5′), 74.2 (*C*H$_2$ of Bn), 73.6 (C-2′), 73.4 (*C*H$_2$ of Bn), 72.3 (C-6), 71.6 (C-3″), 71.1 (C-5″), 70.3 (C-2″), 67.9 (C-4″), 67.6 (C-6′), 66.8 (C-26), 62.1, 61.5 (C-6″), 55.9, 53.7, 48.4, 41.6, 40.5, 39.8, 39.0 (*C*H$_2$ of NPAc), 37.8, 37.1, 36.7, 33.6, 31.6, 31.3, 30.3, 28.8, 28.7, 28.2, 21.3 (*C*H$_3$ of Ac), 20.8, 17.1 (C-27), 16.3 (C-18), 14.4 (C-21), 13.2 (C-19); HRMS (ESI) calcd for $C_{91}H_{99}NO_{22}Na$ [M+Na]$^+$: 1581.6585, found: 1581.6489.

4.3.31. Chlorogenin 3β-*O*-{4-*O*-[2,3,6-tri-*O*-benzoyl-4-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-β-D-glucopyranosyl]-3,6-di-*O*-benzyl-2-*O*-(2-nitro)phenylacetyl-β-D-glucopyranoside} 6α-acetate (47)

According to the general procedure for glycosylation, treatment of **29** (90 mg, 0.09 mmol) and **22** (167 mg, 0.14 mmol) in CH_2Cl_2 afforded **47** (98 mg, 53%) as a white solid: mp 123 °C; $[\alpha]_D^{25}$ +6.8 (*c* 0.07, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.84–8.02 (m, 12H, H-Ar), 7.70 (d, *J* = 7.5 Hz, 2H, H-Ar), 7.62–7.00 (m, 35H, H-Ar), 5.67 (m, 2H, H-4‴, H-2‴), 5.56 (t, *J* = 9.7 Hz, 1H, H-3″), 5.38 (dd, *J* = 8.2, 9.8 Hz, 1H, H-2″), 5.29 (m, 1H, H-3‴), 4.82 (m, 2H, C*H*$_2$ of Bn, H-2′), 4.71 (d, *J* = 8.1 Hz, 1H, H-1″), 4.69 (d, *J* = 7.9 Hz, 1H, H-1‴), 4.61 (m, 1H, H-6), 4.57 (d, *J* = 12.2 Hz, 1H, C*H*$_2$ of Bn), 4.34 (d, 2H, H-16, C*H*$_2$ of Bn), 4.30–4.26 (m, 3H, H-1′, H-6a″, C*H*$_2$ of Bn), 4.17 (m, 1H, H-6b″), 4.08 (d, *J* = 9.5 Hz, 1H, H-4″), 3.91 (t, *J* = 9.2 Hz, 1H, H-4′), 3.77 (m, 3H, H-5‴, C*H*$_2$ of NPAc), 3.67–3.54 (m, 3H, H-6a‴, H-6b‴, H-6a′), 3.51–3.43 (m, 3H, H-3′, H-6b′, H-26a), 3.37–3.29 (m, 3H, H-3, H-26b, H-5″), 3.16 (m, 1H, H-5′), 1.99 (s, 3H, C*H*$_3$ of Ac), 1.92–1.52 (m, 13H), 1.47–1.19 (m, 6H), 1.08–1.06 (m, 3H), 0.93 (d, *J* = 7.0 Hz, 3H, H-21), 0.91–0.81 (m, 3H), 0.80 (s, 3H, H-19), 0.77 (d, *J* = 6.3 Hz, 3H, H-27), 0.72 (s, 3H, H-18), 0.61–0.60 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 170.80, 167.95, 165.71, 165.5, 165.3, 165.2, 165.2, 165.0, 164.8 (OC=O), 149.1, 138.7, 137.8, 137.8, 133.4, 133.3, 133.27, 133.22, 133.08, 133.01, 132.7, 130.8, 129.9–127.7, 127.0, 126.9, 125.2, 124.9, 109.2 (C-22), 100.7 (C-1‴), 100.4 (C-1″), 98.7 (C-1′), 80.7 (C-3′),

80.6 (C-16), 77.7 (C-3), 77.3 (C-4′), 75.6 (C-4″), 74.4 (C-5′), 74.1 (*C*H$_2$ of Bn), 73.5 (C-2′), 73.3 (CH$_2$ of Bn), 72.8 (C-3″), 72.7 (C-5″), 72.3 (C-6), 72.1 (C-2″), 71.7 (C-3‴), 71.2 (C-5‴), 69.7 (C-2‴), 67.5 (C-6′), 67.4 (C-4‴), 66.8 (C-26), 62.3 (C-6″), 62.1, 60.9 (C-6‴), 55.9, 53.7, 48.3, 41.5, 40.5, 39.8, 38.7 (*C*H$_2$ of NPAc), 37.8, 37.0, 36.7, 33.63, 31.65, 31.3, 30.2, 29.6, 28.8, 28.1, 21.3 (CH$_3$ of Ac), 20.8, 17.1 (C-27), 16.3 (C-18), 14.4 (C-21), 14.0 (C-19); HRMS (ESI) calcd for $C_{118}H_{121}NO_{30}Na$ [M+Na]$^+$: 2055.7899, found: 2055.7859.

4.3.32. Chlorogenin 3β-*O*-[4-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-3,6-di-*O*-benzyl-2-*O*-(2-nitro)phenylacetyl-β-D-glucopyranoside] 6α-acetate (48)

According to the general procedure for glycosylation, treatment of **29** (90 mg, 0.09 mmol) and **23** (86 mg, 0.14 mmol) in CH_2Cl_2 afforded **48** (125 mg, 95%) as a white solid: mp 131 °C; $[\alpha]_D^{25}$ +9.0 (*c* 0.06, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.25 (d, *J* = 8.1 Hz, 1H, H-Ar), 8.03 (d, *J* = 7.8 Hz, 2H, H-Ar), 8.03–7.09 (m, 26H, H-Ar), 5.67 (d, *J* = 10.3 Hz, 1H, H-3″), 5.53 (m, 2H, H-2″, H-4″), 5.22 (s, 1H, H-1″), 5.11 (t, *J* = 7.4 Hz, 1H, H-2′), 4.80 (d, *J* = 11.5 Hz, 1H, C*H*$_2$ of Bn), 4.71 (d, *J* = 11.4 Hz, 1H, C*H*$_2$ of Bn), 4.68 (d, *J* = 7.2 Hz, 1H, H-1′), 4.65 (m, 1H, H-6), 4.56 (dd, *J* = 4.5, 12 Hz, 2H, C*H*$_2$ of Bn), 4.36 (dd, *J* = 7.2, 15.4 Hz, 1H, H-16), 4.17–4.15 (m, 2H, H-4′, H-5″), 3.80–3.74 (m, 3H, H-3′, H-6a′, H-6b′), 3.55–3.54 (m, 2H, H-5′, H-3), 3.45–3.43 (m, 1H, H-26a), 3.37 (t, *J* = 10.9 Hz, 1H, H-26b), 2.03 (s, 3H, CH$_3$-Ac), 2.01–1.10 (m, 23H), 0.94 (d, *J* = 6.7 Hz, 3H, H-21), 0.89 (m, 2H), 0.86 (s, 3H, H-19), 0.80 (d, *J* = 6.1 Hz, 3H, C*H*$_3$-6″), 0.77 (d, *J* = 6.1 Hz, 3H, H-27), 0.74 (s, 3H, H-18), 0.67–0.66 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 170.6, 165.7, 165.6, 165.6, 162.9 (OC=O), 146.5, 137.9, 137.6, 133.5, 133.4, 133.2, 133.1, 132.7, 131.0, 130.2–126.7, 125.8, 109.2 (C-22), 98.6 (C-1″), 96.9 (C-1′), 80.6 (C-16), 80.4 (C-3′), 78.0 (C-3), 77.2 (C-2′), 75.1 (C-5′), 74.2 (C-4′), 73.6 (*C*H$_2$ of Bn), 73.0 (*C*H$_2$ of Bn), 72.3 (C-6), 71.5 (C-4″), 71.0 (C-2″), 69.9 (C-3″), 68.2 (C-6′), 67.1 (C-5″), 66.8 (C-26), 62.1, 55.9, 53.7, 48.5, 41.5, 40.5, 39.8 (*C*H$_2$ of NPAc), 37.8, 37.1, 36.7, 33.6, 31.6, 31.3, 30.8, 28.9, 28.7, 28.1, 21.3 (*C*H$_3$ of Ac), 20.8, 17.0 (C-6″), 16.9 (C-27), 16.3 (C-18), 14.4 (C-21), 13.3 (C-19); HRMS (ESI) calcd for $C_{84}H_{95}NO_{20}Na$ [M+Na]$^+$: 1460.6340, found: 1460.6469.

4.3.33. Chlorogenin 3β-*O*-{3,6-di-*O*-benzyl-4-*O*-[4-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl) 2,3-di-*O*-isopropylidene-α-L-rhamnopyranosyl]-2-*O*-(2-nitro) phenylacetyl-β-D-glucopyranoside} 6α-acetate (49)

According to the general procedure for glycosylation, treatment of **29** (90 mg, 0.09 mmol) and **24** (111 mg, 0.14 mmol) in CH_2Cl_2 afforded **49** (68 mg, 46%) as a white solid: mp 136–140 °C; $[\alpha]_D^{25}$ +18.1 (*c* 0.07, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.27 (d, *J* = 7.2 Hz, 1H, H-Ar), 8.08 (d, *J* = 7.0 Hz, 2H, H-Ar), 7.96 (d, *J* = 7.0 Hz, 2H, H-Ar), 7.89 (d, *J* = 7.4 Hz, 1H, H-Ar), 7.80 (d, *J* = 7.1 Hz, 2H, H-Ar), 7.68 (t, *J* = 7.2 Hz, 2H, H-Ar), 7.60–7.14 (m, 19H, H-Ar), 5.73 (dd, *J* = 3.8, 10.9 Hz, 1H, H-3″), 5.70 (dd, *J* = 10.0, 4.4 Hz, 1H, H-3‴), 5.66 (s, 1H, H-2″), 5.61 (s, 1H, H-2‴), 5.56 (t, *J* = 10.4 Hz, 1H, H-4″), 5.54 (t, *J* = 10.4 Hz, 1H, H-4‴), 5.35 (s, 1H, H-1″), 5.28 (s, 1H, H-1‴), 5.08 (d, *J* = 12.0 Hz, 1H, C*H*$_2$ of Bn), 5.01 (d, *J* = 12.0 Hz, 1H, C*H*$_2$ of Bn), 4.70 (m, 1H, H-5″), 4.66 (m, 1H, H-6), 4.65 (d, *J* = 7.6 Hz, 1H, H-1′), 4.63 (d, *J* = 12.4 Hz, 1H, C*H*$_2$ of Bn), 4.58 (d, *J* = 12.0 Hz, 1H, C*H*$_2$ of Bn), 4.37 (q, *J* = 7.2 Hz, 1H, H-16), 4.32 (m, 1H, H-5‴), 4.09 (t, *J* = 8.8 Hz, 1H, H-4′), 3.89–3.81 (m, 4H, H-2′, H-3′, H-6a′, H-6b′), 3.73 (m, 1H, H-3), 3.55 (d, *J* = 9.6 Hz, 1H, H-5′), 3.45 (m, 1H, H-26a), 3.33 (t, *J* = 11.2 Hz, 1H, H-26b), 2.05 (s, 3H, C*H*$_3$ of Ac), 1.95–1.43 (m, 22H), 1.30 (d, *J* = 6.0 Hz, 3H, H-6″), 1.14–1.13 (m, 3H), 0.95 (d, *J* = 5.6 Hz, 3H, H-6‴), 0.94 (d, *J* = 6.4 Hz, 3H, H-21), 0.77 (d, *J* = 7.2 Hz, 3H, H-27), 0.72 (s, 3H, H-19), 0.71 (s, 3H, H-18), 0.66–0.65 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 170.8, 165.9, 165.7, 165.6, 165.5, 164.9, 163.3 (OC=O), 138.0–132.9, 129.9–126.0, 109.2 (C-22), 98.8 (C-1′), 98.0 (C-1″), 97.1 (C-1‴), 84.2 (C-3′), 80.6 (C-16), 76.8 (C-2′), 76.6 (C-3), 74.9 (C-5′), 74.6 (C-4′), 74.5 (*C*H$_2$ of Bn), 73.0 (*C*H$_2$ of Bn), 72.5 (C-6), 71.8 (C-4″), 71.5 (C-4‴), 71.0 (C-2‴), 70.3 (C-2″), 70.1 (C-3‴), 70.0 (C-3″), 68.2 (C-6′), 67.1 (C-5‴), 66.9 (C-5″), 66.8 (C-26), 62.1, 56.0, 53.7, 48.5, 41.6, 40.5, 39.8 (*C*H$_2$ of NPAc), 37.8, 37.1, 36.7, 33.7, 31.6, 31.3, 30.3, 29.0, 28.7, 27.8, 26.3, 21.3 (*C*H$_3$ of Ac), 20.9, 17.4 (C-6″), 17.3 (C-6‴), 17.1 (C-27), 16.4 (C-18), 14.5 (C-21), 13.2 (C-19); HRMS (ESI) calcd for $C_{93}H_{109}NO_{24}Na$ [M+Na]$^+$: 1647.7265, found: 1647.7298.

4.3.34. Chlorogenin 3β-*O*-[2-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-3,6-di-*O*-benzyl-4-*O*-levulinoyl-β-D-glucopyranoside] 6α-acetate (50)

According to the preparation of **29**, **48** (1 g, 0.73 mmol) was treated with hydrazine acetate (101 mg, 1.10 mmol) in CH_2Cl_2/methanol (1:1, 4 mL) to afford **50** (726 mg, 78%) as a off-white solid: mp 133 °C; $[\alpha]_D^{25}$ +51.9 (*c* 0.1, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 7.93 (d, *J* = 7.6 Hz, 2H, H-Ar), 7.84 (d, *J* = 7.7 Hz, 2H, H-Ar), 7.71 (d, *J* = 7.7 Hz, 2H, H-Ar), 7.51–7.01 (m, 19H, H-Ar), 5.69 (s, 1H, H-3″), 5.67 (s, 1H, H-2″), 5.54 (t, *J* = 9.8 Hz, 1H, H-4″), 5.37 (s, 1H, H-1″), 4.86 (d, 1H, *J* = 11.3 Hz, C*H*$_2$ of Bn), 4.74 (d, *J* = 11.4 Hz, 1H, C*H*$_2$ of Bn), 4.62–4.60 (m, 1H, H-5″), 4.56–4.50 (m, 1H, H-6), 4.50 (s, 1H, H-1′), 4.49–4.40 (m, 2H, CH$_2$ of Bn), 4.28 (q, *J* = 7.4 Hz, 1H, H-16), 3.65–3.60 (m, 2H, H-6a′, H-6b′), 3.63–3.61 (m, 2H, H-3, H-2′), 3.55–3.52 (m, 2H, H-3′, H-4′), 3.38–3.37 (m, 1H, H-5′), 3.36–3.34 (m, 1H, H-26a), 3.26 (t, *J* = 10.9 Hz, 1H, H-26b), 1.95 (s, 3H, C*H*$_3$ of Ac), 1.88–1.34 (m, 18H), 1.18–0.82 (m, 6H), 1.22 (d, *J* = 6.0 Hz, 3H, H-6″), 0.86 (d, *J* = 6.8 Hz, 3H, H-21), 0.78 (m, 1H), 0.69 (d, *J* = 6.1 Hz, 3H, H-27), 0.63 (s, 3H, H-19), 0.60 (s, 3H, H-18), 0.57 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 170.8, 166.0, 165.5, 165.4 (OC=O), 138.3, 137.6, 133.3, 133.2, 133.0, 129.8–127.7, 109.2 (C-22), 98.6 (C-1′), 97.8 (C-1″), 85.9 (C-3′) 80.6 (C-16), 76.7 (C-3), 76.5 (C-2′), 75.5, 73.6 (*C*H$_2$ of Bn), 72.9 (C-4′), 72.4 (C-6), 71.8 (C-4″), 70.6 (C-2″), 70.6 (C-6′), 70.0 (C-3″), 66.8 (C-26), 66.7 (C-5″), 62.1, 55.9, 53.7, 48.3, 41.5, 40.5, 39.7, 37.7, 37.1, 36.7, 33.6, 31.6, 31.3, 30.2, 29.1, 28.7, 28.0, 21.3 (*C*H$_3$ of Ac), 20.8, 17.4 (C-6″), 17.1 (C-27), 16.3 (C-19), 14.4 (C-21), 13.1 (C-18); HRMS (ESI) calcd for $C_{76}H_{90}O_{17}Na$ [M+Na]$^+$: 1297.6070, found: 1297.6074.

4.3.35. Chlorogenin 3β-*O*-[2,4-di-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-3,6-di-*O*-benzyl-β-D-glucopyranoside] 6α-acetate (51)

According to the general procedure for glycosylation, treatment of **50** (90 mg, 0.07 mmol) and **23** (66 mg, 0.11 mmol) in CH_2Cl_2 afforded **51** (102 mg, 83%) as a white solid: mp 123 °C; $[\alpha]_D^{25}$ +42.5 (*c* 0.07, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.04 (d, *J* = 8.1 Hz, 2H, H-Ar), 7.91 (d, *J* = 8.1 Hz, 2H, H-Ar), 7.81 (t, *J* = 9.1 Hz, 4H, H-Ar), 7.74 (d, *J* = 8.1 Hz, 2H, H-Ar), 7.68 (t, *J* = 8.2 Hz, 2H, H-Ar), 7.58–6.76 (m, 28H, H-Ar), 5.73 (dd, *J* = 10.9, 3.8 Hz, 1H, H-3″), 5.70 (dd, *J* = 4.4, 10.0 Hz, 1H, H-3‴), 5.66 (s, 1H, H-2″), 5.61 (s, 1H, H-2‴), 5.56 (t, *J* = 10.4 Hz, 1H, H-4″), 5.54 (t, *J* = 10.4 Hz, 1H, H-4‴), 5.35 (s, 1H, H-1″), 5.28 (s, 1H, H-1‴), 5.08 (d, *J* = 12.0 Hz, 1H, C*H*$_2$ of Bn), 5.01 (d, *J* = 12.0 Hz, 1H, C*H*$_2$ of Bn), 4.70 (m, 1H, H-5″), 4.66–4.65 (m, 1H, H-6), 4.65 (d, *J* = 7.6 Hz, 1H, H-1′), 4.63 (d, *J* = 12.4 Hz, 1H, C*H*$_2$ of Bn), 4.58 (d, *J* = 12.0 Hz, 1H, C*H*$_2$ of Bn), 4.37 (q, *J* = 7.2 Hz, 1H, H-16), 4.32 (m, 1H, H-5‴), 4.09 (t, *J* = 8.8 Hz, 1H, H-4′), 3.89–3.81 (m, 4H, H-2′, H-3′, H-6a′, H-6b′), 3.73–3.72 (m, 1H, H-3), 3.55 (d, *J* = 9.6 Hz, 1H, H-5′), 3.45–3.44 (m, 1H, H-26a), 3.33 (t, *J* = 11.2 Hz, 1H, H-26b), 2.08–2.06 (m, 1H), 2.05 (s, 3H, C*H*$_3$ of Ac), 1.93–1.91 (m, 2H), 1.83–1.82 (m, 1H), 1.77–1.39 (m, 15H), 1.30 (d, *J* = 6.0 Hz, 3H, H-6″), 1.28–1.00 (m, 5H), 0.95 (d, *J* = 5.6 Hz, 3H, H-6‴), 0.94 (d, *J* = 6.4 Hz, 3H, H-21), 0.88 (m, 1H), 0.77 (d, *J* = 7.2 Hz, 3H, H-27), 0.72 (s, 3H, H-19), 0.71 (s, 3H, H-18), 0.68–0.67 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz)

δ 170.8, 165.9, 165.7, 165.6, 165.5, 164.9, 163.3 (OC=O), 138.0–132.9, 129.9–126.0, 109.2 (C-22), 98.8 (C-1′), 98.0 (C-1″), 97.1 (C-1‴), 84.2 (C-3′), 80.6 (C-16), 76.8 (C-2′), 76.6 (C-3), 74.9 (C-5′), 74.6 (C-4′), 74.5 (*C*H$_2$ of Bn), 73.0 (*C*H$_2$ of Bn), 72.5 (C-6), 71.8 (C-4″), 71.5 (C-4‴), 71.0 (C-2‴), 70.3 (C-2″), 70.1 (C-3‴), 70.0 (C-3″), 68.2 (C-6′), 67.1 (C-5‴), 66.9 (C-5″), 66.8 (C-26), 62.1, 55.9, 53.7, 48.3, 41.6, 40.5, 39.7, 37.7, 37.2, 36.7, 33.69, 31.68, 31.3, 30.2, 29.1, 28.7, 28.0, 21.3 (*C*H$_3$ of Ac), 20.8, 17.4 (C-6″), 17.3 (C-6‴), 17.16 (C-27), 16.43 (C-18), 14.52 (C-21), 13.20 (C-19); HRMS (ESI) calcd for $C_{103}H_{112}O_{24}Na$ [M+Na]$^+$: 1756.7470, found: 1756.7499.

4.3.36. Chlorogenin 3β-*O*-{3,6-di-*O*-benzyl-2-*O*-(2,3,4-tri-*O*-benzoyl-α-L-rhamnopyranosyl)-4-*O*-[4-*O*-(2,3,4-tri-*O*-benzoyl-α-Lrhamnopyranosyl)-2,3-di-*O*-isopropylidene-α-L-rhamnopyranosyl]-β-D-glucopyranoside] 6α-acetate (52)

According to the general procedure for glycosylation, treatment of **50** (90 mg, 0.07 mmol) and **24** (85 mg, 0.11 mmol) in CH_2Cl_2 afforded **52** (83 mg, 0.04 mmol, 61%) as a white solid: mp 118 °C; $[\alpha]_D^{25}$ +35.3 (*c* 0.2, CH_2Cl_2); ^{1}H NMR ($CDCl_3$, 600 MHz) δ 8.08 (d, *J* = 7.6 Hz, 2H, H-Ar), 7.91 (m, 6H, H-Ar), 7.77 (t, *J* = 8.7 Hz, 4H, H-Ar), 7.60–6.97 (m, 28H, H-Ar), 5.74 (m, 1H, H-3‴), 5.61 (s, 1H, H-2‴), 5.57–5.64 (m, 4H, H-2″, H-4″, H-4‴, H-3″), 5.45 (s, 1H, H-1‴), 5.43 (s, 1H, H-1″), 5.19 (s, 1H, H-1‴), 4.93 (s, 2H, C*H*$_2$ of Bn), 4.71–4.70 (m, 1H, H-5‴), 4.66–4.65 (m, 1H, H-6), 4.63 (d, *J* = 7.8 Hz, 1H, H-1′), 4.62 (s, 2H, C*H*$_2$ of Bn), 4.38 (dd, *J* = 7.3, 14.9 Hz, 1H, H-16), 4.15–4.13 (m, 2H, H-4‴, H-2‴), 3.98–3.95 (m, 2H, H-5″, H-4′), 3.83–3.80 (m, 2H, H-2′, H-5‴), 3.77–3.68 (m, 4H, H-6a′, H-6b′, H-3′, H-3), 3.53–3.45 (m, 3H, H-5′, H-3‴, H-26a), 3.36 (t, *J* = 10.9 Hz, 1H, H-26b), 2.19–1.70 (m, 13H), 1.68 (s, 3H, C(C*H*$_3$)$_2$), 1.60–1.59 (m, 6H), 1.48 (s, 5H, C(C*H*$_3$)$_2$), 1.33 (d, *J* = 6.2 Hz, 3H, H-6‴), 1.27–1.13 (m, 5H), 1.02 (d, *J* = 6.0 Hz, 3H, H-6″), 0.95 (d, *J* = 6.7 Hz, 3H, H-21), 0.87–0.85 (m, 1H), 0.78 (d, *J* = 6.2 Hz, 3H, H-27), 0.72 (s, 3H, H-19), 0.70 (s, 3H, H-18), 0.67–0.66 (m, 1H); ^{13}C NMR ($CDCl_3$, 150 MHz) δ 170.7, 165.9, 165.7, 165.5, 165.3, 165.0, 163.3 (OC=O), 137.8, 137.5, 133.3–132.9, 129.9–127.1, 109.5 (C-22), 109.2 (C(CH$_3$)$_2$), 98.7 (C-1′), 97.9 (C-1‴), 96.9 (C-1‴), 96.5 (C-1″), 84.2 (C-3), 80.6 (C-16), 78.0 (C-4‴), 78.0 (C-3‴), 76.8 (C-2′), 76.5 (C-3′), 76.1 (C-2‴), 75.5 (*C*H$_2$ of Bn), 74.9 (C-5′), 74.4 (C-4′), 73.5 (*C*H$_2$ of Bn), 72.4 (C-6), 71.8 (C-3″), 71.8 (C-4″), 70.8 (C-4‴), 70.4 (C-2″), 70.0 (C-2‴), 69.8 (C-3‴), 69.9 (C-6′), 67.0 (C-5″), 66.8 (C-5‴), 65.1 (C-5‴), 62.1, 55.9, 53.7, 48.3, 41.5, 40.5, 39.7 (CH$_3$), 37.7, 37.1, 36.7, 33.6, 31.6, 31.3, 30.2, 29.1, 28.7, 28.0, 27.8, 26.2, 21.2 (CH$_3$ of Ac), 20.8 (*C*H$_3$), 17.7 (C-6‴), 17.5 (C-6″), 17.4 (C-6‴), 17.0 (C-27), 16.3 (C-19), 14.4 (C-21), 13.1 (C-18); HRMS (ESI) calcd for $C_{112}H_{126}O_{28}Na$ [M+Na]$^+$: 1942.8362, found: 1942.8255.

4.3.37. Chlorogenin 3β-*O*-β-D-glucopyranoside (53)

LiOH (58 mg, 1.39 mmol) was added to a solution of **4** (50 mg, 0.05 mmol) in THF/MeOH (3:1, 4 mL). After stirring overnight at rt, the mixture was concentrated in vacuo and the residue was purified by column chromatography (CH_2Cl_2/methanol, 9:1) to give the crude intermediate. This was then dissolved in CH_2Cl_2/ethanol (1:3, 4 mL) and stirred under H_2 for 12 h with Pd/C (5 mg, 10%) and. The residue was filtered, dried in vacuo, and purified by column chromatography (CH_2Cl_2/methanol, 10:3) to afford **4** (16 mg, 58%) as a white-solid: mp 270 °C; $[\alpha]_D^{25}$ −35.9 (*c* 0.01, MeOH); ^{1}H NMR (pyridine-d_5, 600 MHz) δ 5.10 (d, *J* = 7.7 Hz, 1H, H-1′), 4.56 (m, 2H, H-16, H-6a′), 4.42 (dd, *J* = 5.1, 11.7 Hz, 1H, H-6b′), 4.27 (m, 2H, H-3′, H-4′), 4.08 (m, 2H, H-6, H-2′), 3.91 (m, 1H, H-5′), 3.61 (m, 2H, H-3, H-26a), 3.51 (t, *J* = 10.4 Hz, 1H, H-26b), 2.28–1.19 (m, 19H), 1.16 (d, *J* = 7.0 Hz, 3H, H-21), 1.10–0.89 (m, 6H), 0.86 (s, 3H, H-19), 0.77 (s, 3H, H-18), 0.71 (d, *J* = 5.2 Hz, 3H, H-27), 0.66–0.64 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.6 (C-22), 102.6 (C-1′), 81.5 (C-16), 79.0 (C-5′), 78.8 (C-5′), 78.0 (C-6), 75.8 (C-2′), 72.22 (C-3′), 72.2 (C-4′), 68.9 (C-3), 67.3 (C-26), 64.9 (C-2′), 63.4, 63.3 (C-6′), 56.8, 54.6, 52.6, 43.1, 42.4, 41.2, 40.5, 38.1, 37.0, 34.7, 32.6, 32.2, 31.0, 30.4, 29.9, 29.7, 21.7, 17.7 (C-27), 17.0 (C-19), 15.4 (C-21), 14.0 (C-18); HRMS (ESI) calcd for $C_{33}H_{54}O_9$ [M+Na]$^+$: 617.3661, found: 617.3692.

4.3.38. Chlorogenin 3β-*O*-[2-*O*-(β-L-arabinopyranosyl)-β-D-glucopyranoside] (54)

By the similar procedure of synthesis of **53**, treatment of compound **30** (110 mg, 0.08 mmol) afforded **54** (24 mg, 41%) as a white solid: mp 267 °C; $[\alpha]_D^{25}$ −15.4 (*c* 0.06, MeOH); ^{1}H NMR (pyridine-, 600 MHz) δ 5.41 (d, *J* = 6.1 Hz, 1H, H-1″), 5.11 (d, *J* = 6.1 Hz, 1H, H-1′), 4.63 (t, *J* = 6.4 Hz, 1H, H-2″), 4.56–4.51 (m, 3H, H-16, H-5a″, H-6a′), 4.37–4.37 (m, 2H, H-4″, H-6b′), 4.28–4.24 (m, 3H, H-3″, H-3′, H-4′), 4.16 (d, *J* = 8.4 Hz, 1H, H-2′), 4.07–4.06 (m, 1H, H-6), 3.88 (dd, *J* = 12.1, 2.2 Hz, 1H, H-5b″), 3.82–3.81 (m, 1H, H-5′), 3.63–3.61 (m, 1H, H-3), 3.60–3.58 (m, 1H, H-26a), 3.51 (t, *J* = 10.7 Hz, 1H, H-26b), 3.18 (d, *J* = 12.6 Hz, 1H, OH), 2.25–2.10 (m, 3H), 1.98–1.56 (m, 14H), 1.47–1.22 (m, 6H), 1.16 (d, *J* = 7.0 Hz, 4H, H-21), 1.10–0.90 (m, 2H), 0.86 (s, 3H, H-19), 0.84 (s, 3H, H-18), 0.71 (d, *J* = 5.8 Hz, 3H, H-27), 0.65–0.64 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.7 (C-22), 106.1 (C-1″), 100.7 (C-1′), 83.1 (C-2′), 81.5 (C-16), 78.72 (C-3″), 78.71 (C-5′), 78.6 (C-6), 74.5 (C-3′), 73.5 (C-2″), 71.8 (C-4′), 69.1 (C-4″), 68.8 (C-3), 67.3 (C-26), 66.6 (C-5″), 63.4, 63.0 (C-6′), 56.8, 54.6, 52.7, 43.2, 42.4, 41.2, 40.5, 38.1, 37.0, 34.7, 32.6, 32.2, 31.0, 30.3, 29.7, 29.6, 21.7, 19.7 (C-27), 17.7 (C-19), 17.0 (C-21), 15.5 (C-18); HRMS (ESI) calcd for $C_{38}H_{62}O_{13}Na$ [M+Na]$^+$: 749.4083, found: 749.4051.

4.3.39. Chlorogenin 3β-*O*-[2-*O*-(β-L-fucopyranosyl)-β-D-glucopyranoside] (55)

By the similar procedure of synthesis of **53**, treatment of compound **31** (111 mg, 0.08 mmol) afforded **55** (30 mg, 50%) as a white solid: mp 259 °C; $[\alpha]_D^{25}$ −47.2 (*c* 0.04, MeOH); ^{1}H NMR (pyridine-d_5, 600 MHz) δ 5.20 (d, *J* = 7.8 Hz, 1H, H-1″), 5.06 (d, *J* = 7.7 Hz, 1H, H-1′), 4.55–4.51 (m, 2H, H-16, H-6a′), 4.39–4.36 (m, 2H, H-2″, H-6b′), 4.26 (t, *J* = 9.0 Hz, 1H, H-4′), 4.16–4.01 (m, 5H, H-3′, H-3″, H-2′, H-6, H-4″), 3.85–3.78 (m, 2H, H-5″, H-5′), 3.66–3.65 (m, 1H, H-3), 3.61–3.60 (m, 1H, H-26a), 3.51 (t, *J* = 10.7 Hz, 1H, H-26b), 2.26–2.24 (m, 1H), 2.13–2.10 (m, 2H), 1.98–1.54 (m, 15H), 1.51 (d, *J* = 6.4 Hz, 3H, H-6″), 1.45–1.23 (m, 5H), 1.16 (d, *J* = 7.0 Hz, 3H, H-21), 1.10–0.89 (m, 2H), 0.86 (s, 3H, H-19), 0.85 (s, 3H, H-18), 0.71 (d, *J* = 5.9 Hz, 3H, H-27), 0.66–0.65 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.6 (C-22), 105.4 (C-1″), 101.2 (C-1′), 83.3 (C-2′), 81.5 (C-16), 78.8 (C-6), 78.6 (C-5′), 77.3 (C-3′), 75.5 (C-3″), 73.1 (C-2″), 73.0 (C-4″), 72.2 (C-5″), 71.9 (C-4′), 68.9 (C-3), 67.3, 63.4, 67.3 (C-26), 63.1 (C-6′), 56.8, 54.6, 52.7, 43.2, 42.4, 41.2, 40.5, 38.1, 37.0, 34.7, 32.6, 32.2, 31.0, 30.5, 29.7, 21.7, 17.7 (C-27), 17.6 (C-6″), 17.0 (C-18), 15.4 (C-21), 14.1 (C-19); HRMS (ESI) calcd for $C_{39}H_{64}O_{13}Na$ [M+Na]$^+$: 763.4239, found: 763.4214.

4.3.40. Chlorogenin 3β-*O*-[2-*O*-(β-L-xylopyranosyl)-β-D-glucopyranoside] (56)

By the similar procedure of synthesis of **53**, treatment of compound **32** (110 mg, 0.08 mmol) afforded **56** (35 mg, 60%) as a white solid: mp 262 °C; $[\alpha]_D^{25}$ −25.3 (*c* 0.01, MeOH); ^{1}H NMR (pyridine-d_5, 600 MHz) δ 5.44 (d, *J* = 7.0 Hz, 1H, H-1″), 5.07 (d, *J* = 7.8 Hz, 1H, H-1′), 4.54–4.53 (m, 2H, H-16, H-6a′), 4.43 (d, *J* = 9.5 Hz, 1H, H-5a″), 4.37 (dd, *J* = 5.2, 11.8 Hz, 1H, H-6b′), 4.26–4.21 (m, 3H, H-3′, H-4′, H-4″), 4.16–4.11 (m, 2H, H-2′, H-3″), 4.07–4.02 (m, 2H, H-2″, H-6), 3.81 (m, 1H, H-5′), 3.73 (m, 1H, H-5b″), 3.66 (m, 1H, H-3), 3.60 (d, *J* = 8.8 Hz, 1H, H-26a), 3.51 (t, *J* = 10.6 Hz, 1H, H-26b), 3.18 (d, *J* = 12.4 Hz, 1H, OH), 2.28–2.20 (m, 1H), 2.11–2.06 (m, 2H), 1.98–1.93 (m, 1H), 1.87–1.54 (m, 14H), 1.45–1.43 (m, 2H), 1.16 (d, *J* = 6.8 Hz, 3H, H-21), 1.22–1.09 (m, 4H), 0.88–0.87 (m, 1H), 0.84 (s, 3H, H-19), 0.84 (s, 3H, H-18), 0.71 (d, *J* = 5.3 Hz, 3H,

H-27), 0.65–0.64 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.7 (C-22), 105.0 (C-1′), 101.4 (C-1″), 81.8 (C-3″), 81.5 (C-16), 78.8 (C-6), 78.6 (C-5′), 77.7 (C-4′), 77.1 (C-2′), 75.3 (C-2″), 72.0 (C-3′), 71.3 (C-4″), 69.0 (C-3), 67.3 (C-26), 67.1 (C-5″), 63.4, 63.1 (C-6′), 56.8, 54.6, 52.7, 43.2, 42.5, 41.2, 40.5, 38.2, 37.0, 34.7, 32.6, 32.3, 31.0, 30.5, 29.7, 29.6, 21.7, 17.8 (C-27), 17.1 (C-19), 15.5 (C-21), 14.1 (C-18); HRMS (ESI) calcd for $C_{38}H_{62}O_{13}Na$ [M+Na]$^+$: 749.4083, found: 749.4056.

4.3.41. Chlorogenin 3β-*O*-[2-*O*-(β-D-xylopyranosyl)-β-D-glucopyranoside] (57)

By the similar procedure of synthesis of **53**, treatment of compound **33** (66 mg, 0.05 mmol) afforded **57** (16 mg, 45.3%) as a white solid: mp 260–265 °C; $[\alpha]_D^{25}$ −26.8 (*c* 0.08, MeOH); ^{1}H NMR (pyridine-d_5, 600 MHz) δ 5.33 (d, *J* = 7.1 Hz, 1H, H-1″), 5.11 (d, *J* = 8.0 Hz, 1H, H-1′), 4.56 (dd, *J* = 7.4, 14.7 Hz, 1H, H-16), 4.50–4.46 (m, 2H, H-6a′, H-5a″), 4.37 (dd, *J* = 5.0, 11.8 Hz, 1H, H-6b′), 4.29 (t, *J* = 8.9 Hz, 1H, H-3′), 4.24 (t, *J* = 9.0 Hz, 1H, H-4′), 4.17 (m, 4H, H-4″, H-3″, H-2″, H-2′), 4.06–4.04 (m, 1H, H-6), 3.80–3.67 (m, 2H, H-5′, H-5b″), 3.64–3.62 (m, 1H, H-3), 3.60–3.58 (m, 1H, H-26a), 3.51 (t, *J* = 10.6 Hz, 1H, H-26b), 2.22–2.18 (m, 1H), 2.04–1.94 (m, 3H), 1.83–1.52 (m, 14H), 1.43–1.39 (m, 2H), 1.19–1.17 (m,3H), 1.16 (d, *J* = 6.9 Hz, 3H, H-21), 1.07–1.05 (m, 1H), 0.88–0.86 (m, 1H), 0.85 (s, 3H, H-19), 0.83 (s, 3H, H-18), 0.71 (d, *J* = 5.4 Hz, 3H, H-27), 0.62–0.61 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.6 (C-22), 107.1 (C-1″), 100.8 (C-1′), 84.4 (C-2′), 81.5 (C-16), 78.7 (C-6), 78.68 (C-5′), 78.64 (C-3′), 78.1 (C-3″), 76.3 (C-2″), 71.8 (C-4′), 71.5 (C-4″), 68.9 (C-3), 67.8 (C-5″), 67.3 (C-26), 63.4, 63.0 (C-6′), 56.8, 54.6, 52.7, 43.2, 42.4, 41.2, 40.5, 38.1, 37.0, 34.7, 32.6, 32.2, 31.0, 30.3, 29.7, 29.5, 21.7, 17.7 (C-27), 17.0 (C-19), 15.4 (C-21), 14.0 (C-18); HRMS (ESI) calcd for $C_{38}H_{62}O_{13}Na$ [M+Na]$^+$: 749.4083, found: 749.4077.

4.3.42. Chlorogenin 3β-*O*-[2-*O*-(α-D-mannopyranosyl)-β-D-glucopyranoside] (58)

By the similar procedure of synthesis of **53**, treatment of compound **34** (90 mg, 0.06 mmol) afforded **58** (40 mg, 88%) as a white solid: mp 266 °C; $[\alpha]_D^{25}$ −50.0 (*c* 0.02, MeOH); ^{1}H NMR (pyridine-d_5, 600 MHz) δ 6.18 (s, 1H, H-1″), 5.17–5.15 (m, 1H, H-5″), 5.04 (d, *J* =7.7 Hz, 1H, H-1′), 4.79–4.73 (m, 2H, H-4″, H-2″), 4.68–4.66 (m, 1H, H-3″), 4.60–4.50 (m, 4H, H-6″, H-16, H-6a′, H-6a″), 4.47 (dd, *J* = 5.2, 11.3 Hz, 1H, H-6b″), 4.34 (dd, *J* = 5.5, 11.6 Hz, 1H, H-6b′), 4.22–4.13 (m, 3H, H-2′, H-4′, H-3′), 3.98–3.92 (m, 1H, H-6), 3.82–3.80 (m, 1H, H-5′), 3.59–3.57 (m, 2H, H-3, H-26a), 3.51 (t, *J* = 10.5 Hz, 1H, H-26b), 2.24–2.22 (m, 1H), 2.13–1.94 (m, 3H), 1.83–1.81 (m, 1H), 1.73–1.41 (m, 15H), 1.21–1.20 (m, 3H), 1.16 (d, *J* = 6.9 Hz, 3H, H-21), 1.09–0.88 (m, 2H), 0.85 (s, 3H, H-19), 0.76 (s, 3H, H-18), 0.71 (d, *J* = 5.4 Hz, 3H, H-27), 0.64–0.62 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.6 (C-22), 102.5 (C-1″), 102.4 (C-1′), 81.5 (C-16), 80.2 (C-2′), 78.6 (C-5′), 78.5 (C-6), 77.5 (C-3′), 75.0 (C-5″), 73.5 (C-3″), 72.8 (C-4″), 72.4 (C-4′), 69.8 (C-2″), 68.8 (C-3), 67.3 (C-26), 63.4, 63.6 (C-6″), 63.2 (C-6′), 56.8, 54.5, 52.6, 43.2, 42.4, 41.2, 40.5, 38.1, 36.9, 34.7, 32.6, 32.2, 31.0, 30.5, 29.9, 29.7, 21.7, 17.7 (C-27), 17.0 (C-19), 15.4 (C-21), 14.0 (C-18); HRMS (ESI) calcd for $C_{39}H_{64}O_{14}Na$ [M+Na]$^+$: 779.4188, found: 779.4182.

4.3.43. Chlorogenin 3β-*O*-[2-*O*-(α-D-glucopyranosyl)-β-D-glucopyranoside] (59)

By the similar procedure of synthesis of **53**, treatment of compound **35** (50 mg, 0.03 mmol) afforded **59** (16 mg, 63%) as a white solid: mp 250 °C; $[\alpha]_D^{25}$ −62.5 (*c* 0.08, MeOH); ^{1}H NMR (pyridine-d_5, 600 MHz) δ 5.30 (d, *J* = 7.7 Hz, 1H, H-1″), 5.07 (d, *J* = 7.7 Hz, 1H, H-1′), 4.66–4.63 (m, 2H, H-16, H-6), 4.58–4.54 (bt, *J* = 12.0 Hz, 1H, H-3), 4.52 (dd, *J* = 2.4, 12.0 Hz, 1H, H-6a′), 4.43 (dd, *J* = 12.0, 5.1 Hz, 1H, H-6b′), 4.39–4.36 (m, 2H, H-4′, H-4″), 4.33 (t, *J* = 9.2 Hz, 1H, H-3′), 4.27–4.23 (m, 3H, H-3″, H-26a, H-26b), 4.17–4.14 (m, 2H, H-2′, H-2″), 4.06–4.02 (m, 1H, H-5″), 3.99–3.96 (m, 1H, H-5′), 3.87–3.85 (m, 1H, H-6), 3.66–3.59 (m, 3H, H-6a″, H-6b″), 3.51 (t, *J* = 10.8 Hz, 1H), 3.16 (br d, *J* = 12.6 Hz, 1H), 2.20 (dt, *J* = 8.1, 4.2 Hz, 1H), 2.15–2.08 (m, 2H), 1.98 (t, *J* = 6.7 Hz, 1H), 1.83 (dd, *J* = 8.4, 6.6 Hz, 1H), 1.76–1.67 (m, 3H), 1.63–1.56 (m, 6H), 1.48–1.43 (m, 3H), 1.34–1.24 (m, 7H), 1.15 (d, *J* = 6.7 Hz, 3H, H-21), 1.09–1.06 (m, 1H), 0.84 (s, 3H, H-19), 0.83 (s, 3H, H-18), 0.71 (d, *J* = 5.2 Hz, 3H, H-27), 0.65–0.60 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.7 (C-22), 107.2 (C-1″), 102.2 (C-1′), 85.6, 81.6 (C-16), 80.2, 79.3, 78.7, 78.5, 78.3, 77.5, 72.2, 71.8, 69.1, 67.3 (C-26), 63.5, 63.4, 63.1, 56.8, 54.6, 52.6, 43.1, 42.5, 41.3, 40.6, 38.1, 37.1, 34.7, 32.6, 32.3, 31.1, 30.5, 30.4, 30.2, 29.7, 21.8, 17.8, 17.1, 15.5, 14.1; HRMS (ESI) calcd for $C_{39}H_{64}O_{14}Na$ [M+Na]$^+$: 779.4188, found: 779.4203.

4.3.44. Chlorogenin 3β-*O*-[2-*O*-(β-D-galatopyranosyl)-β-D-glucopyranoside] (60)

By the similar procedure of synthesis of **53**, treatment of compound **36** (52 mg, 0.03 mmol) afforded **60** (13 mg, 0.02 mmol, 49%) as a white solid: mp 250–260 °C; $[\alpha]_D^{25}$ −19.6 (*c* 0.06, MeOH); ^{1}H NMR (pyridine-d_5, 600 MHz) δ 5.18 (d, *J* = 7.8 Hz, 1H, H-1″), 5.08 (d, *J* = 7.6 Hz, 1H, H-1′), 4.61 (t, *J* = 8.0 Hz, 1H, H-2″), 4.58–4.50 (m, 5H, H-16, H-4″, H-6a′, H-6″,), 4.38–4.36 (m, 1H, H-6b′), 4.30 (t, *J* = 8.9 Hz, 1H, H-3′), 4.23 (t, *J* = 8.9 Hz, 1H, H-4′), 4.16–4.13 (m, 5H, H-2′, H-3″, H-5″), 4.04–4.03 (m, 1H, H-6), 3.83–3.80 (m, 1H, H-5′), 3.59–3.56 (m, 2H, H-3, H-26a), 3.51–3.46 (m, 1H, H-26b), 2.19–2.16 (m, 1H), 2.08–2.07 (m, 3H), 1.95–1.94 (m, 1H), 1.80–1.51 (m, 12H), 1.42–1.22 (m, 6H), 1.16 (d, *J* = 6.8 Hz, 3H, H-21), 1.08–1.05 (m, 1H), 0.88–0.84 (m, 1H), 0.85 (s, 3H, H-19), 0.84 (s, 3H, H-18), 0.72 (d, *J* = 5.3 Hz, 3H, H-27), 062–0.60 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.7 (C-22), 107.7 (C-1″), 101.8 (C-1′), 85.56 (C-2′), 81.56 (C-16), 79.7 (C-6), 78.5 (C-5′), 78.2 (C-3′), 78.0 (C-5″), 75.3 (C-3″), 75.0 (C-2″), 71.9 (C-4′), 70.5 (C-4″), 69.0 (C-3), 67.3 (C-26), 63.4, 63.0 (C-6′), 62.6 (C-6″), 56.8, 54.5, 52.6, 50.1, 43.1, 42.4, 41.2, 40.5, 38.0, 37.1, 34.7, 32.6, 32.2, 31.0, 30.1, 29.7, 21.7, 17.8 (C-27), 17.0 (C-19), 15.5 (C-21), 14.1 (C-18); HRMS (ESI) calcd for $C_{39}H_{64}O_{14}Na$ [M+Na]$^+$: 779.4188, found: 779.4216.

4.3.45. Chlorogenin 3β-*O*-[2-*O*-(β-D-lactopyranosyl)-β-D-glucopyranoside] (61)

By the similar procedure of synthesis of **53**, treatment of compound **37** (73 mg, 10.05 mmol) afforded **61** (6 mg, 0.07 mmol, 42%) as a white solid: mp 281 °C; $[\alpha]_D^{25}$ −35.9 (*c* 0.08, MeOH); ^{1}H NMR^{1}H NMR (pyridine-d_5, 600 MHz) δ 6.38 (d, *J* = 8.1 Hz, 1H, H-1‴), 6.36 (d, *J* = 7.3 Hz, 1H, H-1″), 5.08 (d, *J* = 7.5 Hz, 1H, H-1′), 5.07–5.05 (m, 1H, H-5″), 4.88 (s, 1H, H-2‴), 4.70–4.68 (m, 1H, H-3″), 4.65 (s, 1H, H-2″), 4.56–4.54 (m, 4H, H-3‴, H-16, H-6″), 4.53–4.47 (m, 3H, H-6a′, H-5‴, H-4″), 4.38–4.36 (m, 1H, H-6b′), 4.30–4.28 (m, 1H, H-4‴), 4.26 (d, *J* = 7.9 Hz, 1H, H-2′), 4.20–4.16 (m, 2H, H-3′, H-4′), 4.07–4.05 (m, 1H, H-6), 3.79–3.78 (m, 1H, H-5′), 3.68–3.66 (m, 1H, H-3), 3.62–3.58 (m, 1H, H-26a), 3.51 (t, *J* = 10.4 Hz, H-26b), 2.20–2.18 (m, 1H), 2.10–2.09 (m, 2H), 1.98–1.95 (m, 1H), 1.84–1.80 (m, 1H),1.77 (d, *J* = 6.0 Hz, 3H, H-6″), 1.76–1.52 (m, 13H), 1.66–1.62 (m, 2H), 1.45–1.20 (m, 3H), 1.15 (d, *J* = 6.8 Hz, 3H, H-21), 1.09 (s, 3H, H-19), 1.08–0.88 (m, 2H), 0.81 (s, 3H, H-18), 0.70 (d, *J* = 5.4 Hz, 3H, H-27), 0.62–0.61 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.6 (C-22), 103.3 (C-1‴), 102.1 (C-1″), 100.1 (C-1′), 81.5 (C-16), 80.3 (C-4″), 80.0 (C-3′), 78.6 (C-5′), 77.9 (C-2′), 77.7 (C-6), 74.6 (C-4‴), 74.0 (C-3″), 73.4 (C-2″), 73.2 (C-3‴), 73.0 (C-2‴), 72.2 (C-4′), 70.6 (C-5‴), 68.9 (C-3), 67.9 (C-5″), 67.3 (C-26), 63.4 (C-6′), 63.0, 62.9, 56.7, 55.5, 54.5, 52.6, 43.1, 42.4, 41.2, 40.5, 38.0, 37.0, 34.7, 31.0, 30.3, 30.1, 29.7, 21.7, 19.6 (C-6″), 19.0 (C-6‴), 17.7 (C-27), 17.1 (C-18), 15.5

(C-21), 14.2 (C-19); HRMS (ESI) calcd for $C_{45}H_{74}O_{17}Na$ [M+Na]$^+$: 909.4818, found: 909.4884.

4.3.46. Chlorogenin 3β-*O*-[2-*O*-(α-L-rhamnopyranosyl)-β-D-glucopyranoside] (62)

By the similar procedure of synthesis of **53**, treatment of compound **38** (90 mg, 0.07 mmol) afforded **62** (34 mg, 0.05 mmol, 70.0%) as a white solid: mp 219 °C; $[\alpha]_D^{25}$ −39.9 (*c* 0.05, MeOH); ^{1}H NMR (pyridine-d_5, 600 MHz) δ 6.35–6.33 (m, 1H, H-1″), 5.10 (d, *J* = 7.7 Hz, 1H, H-1′), 5.04 (m, 1H, H-5″), 4.76 (m, 1H, H-2″), 4.61 (dd, *J* = 3.4, 9.3 Hz, 1H, H-3″), 4.56 (dd, *J* = 7.3, 14.9 Hz, 1H, H-16), 4.50 (dd, *J* = 2.0, 11.8 Hz, 1H, H-6a′), 4.35 (m, 2H, H-6b′, H-4″), 4.27 (t, *J* = 8.2 Hz, 1H, H-2′), 4.21 (t, *J* = 9.0 Hz, 1H, H-3′), 4.16 (t, *J* = 9.0 Hz, 1H, H-4′), 4.11 (m, 1H, H-6), 3.79 (m, 1H, H-5′), 3.60 (m, 2H, H-3, H-26a), 3.51 (t, *J* = 10.7 Hz, 1H, H-26b), 2.23–1.79 (m, 8H), 1.69–1.38 (m, 13H), 1.80 (d, *J* = 6.2 Hz, 3H, H-6″), 1.25–1.22 (m, 2H), 1.16 (d, *J* = 6.9 Hz, 3H, H-21), 1.08–1.06 (m, 1H), 0.97 (s, 3H, H-19), 0.88–0.86 (m, 1H), 0.85 (s, 3H, H-18), 0.71 (d, *J* = 5.4 Hz, 3H, H-27), 0.64–0.62 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.6 (C-22), 102.6 (C-1″), 100.0 (C-1′), 81.5 (C-16), 80.0 (C-3′), 78.6 (C-5′), 78.5 (C-2′), 77.4 (C-6), 74.6 (C-4″), 73.2 (C-3″), 72.9 (C-2″), 72.2 (C-4′), 69.8 (C-5″), 68.9 (C-3), 67.3 (C-26), 63.5, 63.1 (C-6′), 56.8, 54.5, 52.6, 43.1, 42.4, 41.2, 40.5, 38.2, 37.1, 34.7, 32.6, 32.3, 31.0, 30.3, 29.7, 29.4, 21.7, 19.1 (C-6″), 17.8 (C-27), 17.0 (C-18), 15.5 (C-21), 14.1 (C-19); HRMS (ESI) calcd for $C_{39}H_{64}O_{13}Na$ [M+Na]$^+$: 763.4239, found: 763.4254.

4.3.47. Chlorogenin 3β-*O*-{2-*O*-[4-*O*-(α-L-rhamnopyranosyl)-α-L-rhamnopyranosyl]-β-D-glucopyranoside} (63)

To a solution of **39** (73 mg, 10.05 mmol) in acetic acid (80%, 4 mL) was stirred at 60 °C for 24 h. The mixture was concentrated under vacuum and purified by column chromatography on silica gel (EtOAc/hexane, 2:1), and the crude was then followed the similar method for the preparation of **53**. **63** (6 mg, 0.07 mmol, 41%) was obtained as a white solid: mp 250 °C; $[\alpha]_D^{25}$ −33.7 (*c* 0.02, MeOH); ^{1}H NMR (pyridine-d_5, 600 MHz) δ 6.38 (s, 1H, H-1‴), 6.36 (s, 1H, H-1″), 5.08 (d, *J* = 7.5 Hz, 1H, H-1′), 5.06–4.95 (m, 1H, H-5″), 4.88 (s, 1H, H-2‴), 4.71–4.68 (m, 1H, H-3″), 4.65 (s, 1H, H-2″), 4.56–4.55 (m, 2H, H-3‴, H-16), 4.50–4.38 (m, 3H, H-6a′, H-5‴, H-4″), 4.36–4.32 (m, 1H, H-6b′), 4.30–4.28 (m, 1H, H-4‴), 4.26 (d, *J* = 7.9 Hz, 1H, H-2′), 4.18–4.12 (m, 2H, H-3′, H-4′), 4.06–4.02 (m, 1H, H-6), 3.78–3.77 (m, 1H, H-5′), 3.68–3.66 (m, 1H, H-3), 3.60–3.58 (m, 1H, H-26α), 3.51 (t, *J* = 10.4 Hz, H-26β), 2.20–1.80 (m, 6H), 1.74–1.57 (m, 6H), 1.48–1.18 (m, 12H), 1.66 (d, *J* = 6.3 Hz, 3H, H-6‴), 1.15 (d, *J* = 6.8 Hz, 3H, H-21), 1.09 (s, 3H, H-19), 0.89–0.85 (m, 1H), 0.81 (s, 3H, H-18), 0.70 (d, *J* = 5.4 Hz, 3H, H-27), 0.65–0.55 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.6 (C-22), 103.3 (C-1‴), 102.1 (C-1″), 100.1 (C-1′), 80.3 (C-16), 80.0 (C-4″), 78.6 (C-3′), 77.9 (C-5′), 77.7 (C-2′), 74.6 (C-6), 74.0 (C-4‴), 73.4 (C-3″), 73.2 (C-2″), 73.0 (C-3‴), 72.2 (C-2‴), 70.6 (C-4′), 68.9 (C-5‴), 67.9 (C-3), 67.3 (C-5″), 64.9 (C-26), 63.4 (C-6′), 63.1, 56.8, 54.7, 52.6, 43.3, 42.4, 41.2, 38.2, 37.1, 34.7, 32.6, 32.3, 34.7, 32.6, 31.0, 30.4, 29.7, 21.7, 19.3 (C-6″), 19.1 (C-6‴), 17.7 (C-27), 17.0 (C-18), 15.4 (C-21), 14.0 (C-19); HRMS (ESI) calcd for $C_{45}H_{74}O_{17}Na$ [M+Na]$^+$: 909.4818, found: 909.4884.

4.3.48. Chlorogenin 3β-*O*-[2,4-di-*O*-(α-L-rhamnopyranosyl)-β-D-glucopyranoside] (2)[22]

By the similar procedure of synthesis of **53,** treatment of **51** (102 mg, 0.06 mmol) afforded **2** (38 mg, 73%) as a white solid: mp 247 °C; $[\alpha]_D^{25}$ −72.5 (*c* 0.06, MeOH); The NMR data are similar to the Ref.[22]. HRMS (ESI) calcd for $C_{45}H_{74}O_{17}Na$ [M+Na]$^+$: 909.4818, found: 909.4884.

4.3.49. Chlorogenin 3β-*O*-[4-*O*-(β-L-arabinopyranosyl)-β-D-glucopyranoside] (64)

By the similar procedure of synthesis of **53**, treatment of compound **40** (115 mg, 0.08 mmol) afforded **64** (25 mg, 43%) as a white solid: mp 275–285 °C; $[\alpha]_D^{25}$ −29.8 (*c* 0.09, MeOH); ^{1}H NMR (pyridine-d_5, 600 MHz) δ 5.07 (d, *J* = 7.6 Hz, 1H, H-1″), 5.02 (d, *J* = 7.7 Hz, 1H, H-1′), 4.55 (m, 3H, H-6a′, H-16, H-2″), 4.47 (d, *J* = 11.5 Hz, 1H, H-6b′), 4.38 (t, *J* = 9.3 Hz, 1H, H-4′), 4.27 (m, 3H, H-5a″, H-3′, H-4″), 4.13 (dd, *J* = 2.4, 8.8 Hz, 1H, H-3″), 4.08 (t, *J* = 8.3 Hz, 1H, H-2′), 4.02 (m, 1H, H-6), 3.77 (m, 2H, H-5′, H-5b″), 3.60 (m, 2H, H-3, H-26a), 3.51 (t, *J* = 10.6 Hz, 1H, H-26b), 2.21–2.19 (m, 1H), 2.06–2.04 (m, 2H), 1.96–1.94 (m, 1H), 1.80–1.78 (m, 1H), 1.72–1.39 (m, 16H), 1.20–1.16 (m, 2H), 1.16 (d, *J* = 6.9 Hz, 3H, H-21), 1.06–1.04 (m, 1H), 0.89–0.88 (m, 1H), 0.86 (s, 3H, H-19), 0.77 (s, 3H, H-18), 0.71 (d, *J* = 5.2 Hz, 3H, H-27), 0.63–0.61 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.67 (C-22), 106.1 (C-1″), 102.4 (C-1′), 81.5 (C-16), 81.2 (C-4′), 78.2 (C-6), 76.9 (C-3′), 76.9 (C-5′), 75.5 (C-2′), 75.0 (C-3″), 72.9 (C-2″), 70.0 (C-4″), 68.8 (C-3), 68.2 (C-5″), 67.3 (C-26), 63.4, 62.2 (C-6′), 56.8, 54.6, 52.6, 50.1, 43.1, 42.4, 41.2, 40.5, 38.1, 37.0, 34.7, 32.6, 32.2, 31.0, 30.3, 29.9, 21.7, 17.7 (C-27), 17.0 (C-19), 15.4 (C-21), 14.0 (C-18); HRMS (ESI) calcd for $C_{38}H_{62}O_{13}Na$ [M+Na]$^+$: 749.4083, found: 749.4076.

4.3.50. Chlorogenin 3β-*O*-[4-*O*-(β-L-fucopyranosyl)-β-D-glucopyranoside] (65)

By the similar procedure of synthesis of **53**, treatment of compound **41** (60 mg, 0.04 mmol) afforded **65** (20 mg, 65%) as a white solid: mp 268 °C; $[\alpha]_D^{25}$ −16.9 (*c* 0.08, MeOH); ^{1}H NMR (pyridine-d_5, 600 MHz) δ 5.26 (d, *J* = 7.8 Hz, 1H, H-1″), 5.00 (d, *J* = 7.2 Hz, 1H, H-1′), 4.58–4.56 (m, 2H, H-16, H-6a′), 4.48 (t, *J* = 9.6 Hz, 1H, H-2″), 4.44 (dd, *J* = 12.0, 4.8 Hz, 1H, H-6b′), 4.32–4.29 (m, 2H, H-4′, H-4″) 4.11 (dd, *J* = 9.6, 3.6 Hz, 1H, H-3″), 4.09–4.02 (m, 3H, H-2′, H-3′, H-6), 3.86–3.83 (m, 2H, H-5″, H-5′), 3.64–3.62 (m, 1H, H-3), 3.60–3.58 (m, 1H, H-26a), 3.52 (t, *J* = 10.8 Hz, 1H, H-26b), 3.12 (d, *J* = 12.8 Hz, 1H, OH), 2.10–2.06 (m, 1H), 1.98–1.85 (m, 3H), 1.76–1.56 (m, 15H), 1.54 (d, *J* = 6.6 Hz, 3H, H-6″), 1.48–1.45 (m, 2H), 1.23–1.21 (m, 2H), 1.10–1.08 (m, 1H), 1.16 (d, *J* = 6.6 Hz, 3H, H-21), 0.91–0.89 (m, 1H), 0.86 (s, 3H, H-19), 0.76 (s, 3H, H-18), 0.71 (d, *J* = 6.0 Hz, 3H, H-27), 0.66–0.65 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.7 (C-22), 107.4 (C-1″), 102.5 (C-1′), 81.7 (C-4″), 81.5 (C-16), 78.3 (C-3′), 78.3 (C-4′), 77.1 (C-5′), 75.8 (C-3″), 75.4 (C-2′), 73.9 (C-2″), 73.0 (C-6), 72.4 (C-5″), 68.9 (C-3), 67.3 (C-26), 63.4, 63.1 (C-6′), 56.8, 54.6, 52.6, 43.1, 42.5, 41.2, 40.5, 38.1, 37.0, 34.7, 32.6, 31.0, 31.0, 30.4, 29.9, 29.7, 21.7, 18.5 (C-6″), 18.4 (C-27), 17.8 (C-19), 16.2 (C-21), 14.8 (C-18); HRMS (ESI) calcd for $C_{39}H_{64}O_{13}Na$ [M+Na]$^+$: 763.4239, found: 763.4251.

4.3.51. Chlorogenin 3β-*O*-[4-*O*-(β-L-xylopyranosyl)-β-D-glucopyranoside] (66)

By the similar procedure of synthesis of **53**, treatment of compound **42** (72 mg, 0.05 mmol) afforded **66** (22 mg, 60%) as white solids: mp 310 °C; $[\alpha]_D^{25}$ −13.5 (*c* 0.05, MeOH); ^{1}H NMR (pyridine-d_5, 600 MHz) δ 5.38 (d, *J* = 7.6 Hz, 1H, H-1″), 5.02 (d, *J* = 7.7 Hz, 1H, H-1′), 4.58–4.56 (m, 2H, H-16, H-6a′), 4.44 (m, 1H, H-6b′), 4.36–4.31 (m, 3H, H-3′, H-4′, H-5a″), 4.21 (m, 1H, H-4″), 4.17 (t, *J* = 8.8 Hz, 1H, H-3″), 4.11–4.05 (m, 3H, H-2″, H-6, H-2′), 3.87 (m, 1H, H-5′), 3.71 (t, *J* = 10.7 Hz, 1H, H-5b″), 3.61 (m, 1H, H-3), 3.59 (m, 1H, H-26a), 3.51 (t, *J* = 10.7 Hz, 1H, H-26b), 3.13 (d, *J* = 12.6 Hz, 1H, OH), 2.23 (m, 1H), 2.09–2.07 (m, 3H), 1.98–1.97 (m, 1H), 1.84–1.80 (m, 1H), 1.74–1.44 9 (m, 15H), 1.20–1.19 (m, 2H), 1.16 (d, *J* = 7.0 Hz, 3H, H-21), 1.11–1.08 (m, 1H), 0.90–0.87 (m, 1H), 0.86 (s, 3H, H-19), 0.75 (s, 3H, H-18), 0.71 (d, *J* = 5.8 Hz, 3H, H-27), 0.66–0.65 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.7 (C-22). 107.5 (C-1″), 102.4 (C-1′), 81.5 (C-16), 81.5 (C-4′), 78.9 (C-3″), 78.39 (C-3′), 78.31 (C-2′), 77.2 (C-5′), 76.6 (C-2″), 75.4

(C-6), 71.4 (C-4″), 68.9 (C-3), 68.1 (C-5″), 67.3 (C-26), 63.4, 62.9 (C-6′), 56.8, 54.6, 52.6, 43.1, 42.5, 41.2, 40.5, 38.1, 37.0, 34.7, 32.6, 32.3, 31.0, 30.3, 29.9, 29.7, 21.7, 17.8 (C-27), 17.0 (C-19), 15.5 (C-21), 14.0 (C-18); HRMS (ESI) calcd for $C_{38}H_{62}O_{13}Na$ $[M+Na]^+$: 749.4083, found: 749.4055.

4.3.52. Chlorogenin 3β-*O*-[4-*O*-(β-D-xylopyranosyl)-β-D-glucopyranoside] (67)

By the similar procedure of synthesis of **53**, treatment of compound **43** (74 mg, 0.05 mmol) afforded **67** (15 mg, 40%) as a white solid: mp 229 °C; $[\alpha]_D^{25}$ −27.5 (*c* 0.04, MeOH); ^1H NMR (pyridine-d_5, 600 MHz) δ 5.16 (d, *J* = 7.8 Hz, 1H, H-1″), 5.04 (d, *J* = 7.8 Hz, 1H, H-1′), 4.58 (m, 2H, H-6a′, H-16), 4.50 (d, *J* = 11.5 Hz, 1H, H-6b′), 4.37 (t, *J* = 9.2 Hz, 1H, H-4′), 4.27 (m, 2H, H-3′, H-5a″), 4.18 (m, 1H, H-4″), 4.14 (t, *J* = 8.8 Hz, 1H, H-3″), 4.10 (t, *J* = 8.2 Hz, 1H, H-2′), 4.04 (m, 2H, H-2″, H-6), 3.83 (m, 1H, H-5′), 3.69 (t, *J* = 10.6 Hz, 1H, H-5b″), 3.61 (m, 2H, H-3, H-26a), 3.51 (t, *J* = 10.5 Hz, 1H, H-26b), 2.21–2.18 (m, 1H), 2.06–2.05 (m, 2H), 1.95–1.94(m, 1H), 1.82–1.80 (m, 1H), 1.73–1.39 (m, 14H), 1.19–1.18 (m,3H), 1.16 (d, *J* = 6.9 Hz, 3H, H-21), 1.06–0.89 (m, 2H), 0.86 (s, 3H, H-19), 0.77 (s, 3H, H-18), 0.71 (d, *J* = 5.3 Hz, 3H, H-27), 0.64–0.62 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.6 (C-22), 106.0 (C-1″), 102.4 (C-1′), 81.5 (C-16), 81.4 (C-4′), 78.8 (C-3″), 78.3 (C-6), 76.9 (C-3′), 76.9 (C-5′), 75.5 (C-2′), 75.4 (C-2″), 71.3 (C-4″), 68.8 (C-3), 67.8 (C-5″), 67.3 (C-26), 63.4, 62.2 (C-6′), 56.8, 54.6, 52.2, 43.1, 42.4, 41.2, 40.5, 38.1, 37.0, 34.7, 32.6, 32.2, 31.0, 30.4, 29.9, 29.7, 21.7, 17.7 (C-27), 17.0 (C-19), 15.4 (C-21), 14.0 (C-18); HRMS (ESI) calcd for $C_{38}H_{62}O_{13}Na$ $[M+Na]^+$: 749.4083, found: 749.4082.

4.3.53. Chlorogenin 3β-*O*-[4-*O*-(α-D-mannopyranosyl)-β-D-glucopyranoside] (68)

By the similar procedure of synthesis of **53**, treatment of compound **44** (100 mg, 0.06 mmol) afforded **68** (22 mg, 45%) as white solids: mp 290 °C; $[\alpha]_D^{25}$ +2.5 (*c* 0.04, MeOH); ^1H NMR (pyridine-d_5, 600 MHz) δ 6.54 (d, *J* = 3.3 Hz, 1H, H-1″), 4.97 (d, *J* = 7.8 Hz, 1H, H-1′), 4.91–4.90 (m, 1H, H-2″), 4.71 (d, *J* = 11.2 Hz, 1H, H-6a″), 4.68–4.63 (m, 3H, H-3″, H-4″, H-5″), 4.60 (t, *J* = 9.4 Hz, 1H, H-4′), 4.56 (q, *J* = 7.5 Hz, 1H, H-16), 4.42–4.38 (m, 3H, H-6a′, H-6b′, H-6b″), 4.29 (t, *J* = 9.4 Hz, 1H, H-3′), 4.01–3.99 (m, 1H, H-6), 3.96 (dd, *J* = 9.4, 8.1 Hz, 1H, H-2′), 3.71–3.69 (m, 1H, H-5′), 3.61–3.57 (m, 2H, H-3, H-26a), 3.51 (t, *J* = 10.6 Hz, 1H, H-26b), 3.11 (d, *J* = 12.5 Hz, 1H, OH), 2.23–2.21 (m, 1H), 2.12–1.96 (m, 3H), 1.83–1.80 (m, 1H), 1.74–1.43 (m, 15H), 1.34–1.18 (m, 3H), 1.16 (d, *J* = 6.9 Hz, 3H, H-21), 1.09–1.08 (m, 1H), 0.88–0.87 (m, 1H), 0.86 (s, 3H, H-19), 0.75 (s, 3H, H-18), 0.71 (d, *J* = 6.9 Hz, 3H, H-27), 0.65–0.64 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.7 (C-22), 103.3 (C-1″), 102.3 (C-1′), 81.5 (C-16), 79.2 (C-3′), 78.1 (C-6), 77.0 (C-5′), 76.8 (C-5″), 76.4 (C-4′), 75.9 (C-2′), 73.7 (C-4″), 73.0 (C-2″), 69.8 (C-3″), 68.9 (C-3), 67.3 (C-26), 63.7 (C-6″), 63.4, 62.4 (C-6′), 56.8, 54.6, 52.6, 50.1, 43.1, 42.4, 41.2, 40.5, 38.1, 37.0, 34.7, 32.6, 32.2, 31.0, 30.3, 29.7, 21.7, 17.8 (C-27), 17.0 (C-19), 15.5 (C-21), 14.0 (C-18); HRMS (ESI) calcd for $C_{39}H_{64}O_{14}Na$ $[M+Na]^+$: 779.4188, found: 779.4186.

4.3.54. Chlorogenin 3β-*O*-[4-*O*-(β-D-glucopyranosyl)-β-D-glucopyranoside] (69)

By the similar procedure of synthesis of **53**, treatment of compound **45** (92 mg, 0.06 mmol) afforded **69** (20 mg, 45%) as a white solid: mp 278 °C; $[\alpha]_D^{25}$ −32.7 (*c* 0.02, MeOH); ^1H NMR (pyridine-d_5, 600 MHz) δ 5.22 (d, *J* = 7.9 Hz, 1H, H-1″), 5.02 (d, *J* = 7.7 Hz, 1H, H-1′), 4.90 (dd, *J* = 4.2, 1.8 Hz, 1H, H-4″), 4.64–4.58 (m, 2H, H-5″, H-6a″), 4.57–4.52 (m, 2H, H-6, H-4″), 4.48 (dd, *J* = 2.4, 12 Hz, 1H, H-6b″), 4.40–4.36 (m, 3H, H-4′, H-6b″, H-16), 4.37–4.35 (m, 1H, H-5′), 4.34 (t, *J* = 11.0 Hz, 1H, H-6b′), 4.34–4.31 (m, 1H, H-5′), 4.28 (t, *J* = 12 Hz, 1H, H-6a′), 4.24–4.22 (m, 2H, H-3′, H-3″), 4.13 (dd, *J* = 7.9, 9.0 Hz, H-2′), 4.08–3.98 (m, 3H, H-2″, H-3), 3.85–3.83 (m, 1H), 3.59 (dd, 1H, *J* = 12, 4.8 Hz, H-26a), 3.50 (t, *J* = 12 Hz, 1H, H-26b), 2.14–2.11 (m, 2H), 2.05–1.81 (m, 5H), 1.72–1.45 (m, 16H), 1.16 (d, *J* = 6.7 Hz, 3H, H-21), 1.10–1.06 (m, 2H), 0.86 (s, 3H, H-19), 0.77 (s, 3H, H-18), 0.71 (d, *J* = 5.3 Hz, 3H, H-27), 0.67–0.64 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.6 (C-22), 105.3 (C-1″), 102.3 (C-1′), 81.6, 81.5, 78.8, 78.6, 78.2, 77.2, 76.7, 75.9, 75.3, 75.2, 75.0, 73.6, 71.9, 71.5, 68.8, 67.2, 65.7, 64.8, 63.4, 62.9, 62.5, 56.7, 54.5, 52.6, 43.1, 42.4, 41.2, 40.4, 38.1, 37.0, 34.6, 32.5, 32.2, 31.0, 29.9, 29.6, 21.7, 17.7, 17.0, 15.4, 14.0; HRMS (ESI) calcd for $C_{39}H_{64}O_{14}Na$ $[M+Na]^+$: 779.4188, found: 779.4201.

4.3.55. Chlorogenin 3β-*O*-[4-*O*-(β-D-galatopyranosyl)-β-D-glucopyranoside] (70)

By the similar procedure of synthesis of **53**, treatment of compound **46** (49 mg, 0.03 mmol) afforded **70** (10 mg, 42%) as a white solid: mp 285 °C; $[\alpha]_D^{25}$ −17.5 (*c* 0.04, MeOH); ^1H NMR (pyridine-d_5, 600 MHz) δ 5.13 (d, *J* = 7.6 Hz, 1H, H-1″), 5.02 (d, *J* = 7.8 Hz, 1H, H-1′), 4.57–4.53 (m, 3H, H-16, H-2″, H-6a′), 4.50–4.46 (m, 3H, H-6b′, H-4″, H-6a″), 4.42–4.39 (m, 1H, H-6b″), 4.35 (t, *J* = 8.9 Hz, 1H, H-4′), 4.26 (t, *J* = 8.8 Hz, 1H, H-3′), 4.17–4.12 (m, 2H, H-3″, H-5″), 4.07 (d, *J* = 8.2 Hz, 1H, H-2′), 4.01–3.98 (m, 1H, H-6), 3.85–3.82 (m, 1H, H-5′), 3.60–3.55 (m, 2H, H-3, H-26a), 3.51 (t, *J* =10.5 Hz, 1H, H-26b), 2.25–2.07 (m, 3H), 1.98–1.83 (m, 2H), 1.72–1.45 (m, 15H), 1.34–1.20 (m, 3H), 1.16 (d, *J* = 6.7 Hz, 3H, H-21), 1.09–0.92 (m, 2H), 0.86 (s, 3H, H-19), 0.76 (s, 3H, H-18), 0.71 (d, *J* = 5.0 Hz, 3H, H-27), 0.66–0.65 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.6 (C-22), 106.3 (C-1″), 102.4 (C-1′), 82.6 (C-4′), 81.5 (C-16), 78.2 (C-6), 77.7 (C-5″), 77.1 (C-3′), 76.7 (C-5′), 75.6 (C-3″), 75.4 (C-2′), 72.9 (C-2″), 70.5 (C-4″), 68.8 (C-3), 67.3 (C-26), 63.4, 62.7 (C-6′), 62.5 (C-6″), 56.8, 54.6, 52.6, 43.1, 42.4, 41.2, 40.5, 38.1, 37.0, 34.7, 32.6, 32.2, 31.0, 30.3, 29.9, 29.7, 21.7, 17.7 (C-27), 17.0 (C-19), 15.4 (C-21), 14.0 (C-18); HRMS (ESI) calcd for $C_{39}H_{64}O_{14}Na$ $[M+Na]^+$: 779.4188, found: 779.4187.

4.3.56. Chlorogenin 3β-*O*-[4-*O*-(β-D-lactopyranosyl)-β-D-glucopyranoside] (71)

By the similar procedure of synthesis of **53**, treatment of compound **47** (98 mg, 0.05 mmol) afforded **71** (14 mg, 32%) as white solids: mp 307–315 °C; $[\alpha]_D^{25}$ −31.0 (*c* 0.06, MeOH); ^1H NMR (pyridine-d_5, 600 MHz) δ 5.19 (d, *J* = 8.1 Hz, 1H, H-1″), 5.07 (d, *J* = 7.7 Hz, 1H, H-1‴), 5.01 (d, *J* = 7.7 Hz, 1H, H-1′), 4.46–4.59 (m, 8H, H-16, H-6a′, H-6b′, H-6a″, H-6b″, H-2‴, H-4‴, H-6a‴), 4.41–4.39 (m, 1H, H-6b‴), 4.34 (t, *J* = 9.0 Hz, 1H, H-4′), 4.28–4.25 (m, 3H, H-4″, H-3″, H-3′), 4.15–4.09 (m, 3H, H-3‴, H-5‴, H-2″), 4.05–4.01 (m, 3H, H-6, H-2′, H-5″), 3.85–3.79 (m, 1H, H-5′), 3.59–3.58 (m, 2H, H-3, H-26a), 3.51–3.48 (m, 1H, H-26b), 2.24–2.23 (m, 1H), 2.13–1.95 (m, 3H), 1.84–1.80 (m, 1H), 1.73–1.44 (m, 15H), 1.32–1.18 (m, 3H), 1.16 (d, *J* = 6.9 Hz, 3H, H-21), 1.08–0.92 (m, 2H), 0.86 (s, 3H, H-19), 0.76 (s, 3H, H-18), 0.71 (d, *J* = 5.5 Hz, 3H, H-27), 0.67–0.65 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.6 (C-22), 106.2 (C-1‴), 104.9 (C-1″), 102.4 (C-1′), 82.0 (C-4″), 81.56 (C-4′), 81.53 (C-16), 78.2 (C-6), 77.7 (C-5‴), 77.1 (C-5″), 76.9 (C-3′), 76.8 (C-3″), 76.7 (C-5′), 75.6 (C-3‴), 75.3 (C-2′), 74.7 (C-2″), 72.8 (C-2‴), 70.5 (C-4‴), 68.8 (C-3), 67.3 (C-26), 63.4, 62.5 (C-6′), 62.4 (C-6″), 62.2 (C-6‴), 56.8, 54.5, 52.6, 43.1, 42.4, 41.2, 40.5, 38.1, 37.0, 34.7, 32.6, 32.2, 30.9, 30.3, 29.9, 29.7, 21.7, 17.7 (C-27), 17.0 (C-19), 15.4 (C-21), 14.0 (C-18); HRMS (ESI) calcd for $C_{45}H_{74}O_{19}Na$ $[M+Na]^+$: 941.4717, found: 941.4797.

4.3.57. Chlorogenin 3β-*O*-[4-*O*-(α-L-rhamnopyranosyl)-β-D-glucopyranoside] (72)

By the similar procedure of synthesis of **53**, treatment of compound **48** (125 mg, 0.09 mmol) afforded **72** (40 mg, 62%) as a white solid: mp 229 °C; $[\alpha]_D^{25}$ −66.1 (*c* 0.06, MeOH); ^1H NMR (pyridine-d_5, 600 MHz) δ 5.88 (s, 1H, H-1″), 5.00 (d, *J* = 7.8 Hz, 1H, H-1′), 4.98 (m, 1H, H-5″), 4.70 (d, *J* =1.3 Hz, 1H, H-2″), 4.57–4.50 (m, 2H, H-3″,

H-16), 4.45–4.39 (m, 1H, H-4′), 4.35 (t, J = 9.4 Hz, 1H, H-4″), 4.26 (d, J = 11.3 Hz, 1H, H-6a′), 4.15–4.05 (m, 2H, H-3′, H-6b′), 4.00–3.87 (m, 2H, H-6, H-2′), 3.69–3.50 (m, 3H, H-3, H-5′, H-26α), 3.51–3.48 (m, 1H, H-26β), 2.24–2.19 (m, 2H), 2.11–1.83 (m, 5H), 1.73 (d, J = 6.2 Hz, 3H, H-6″), 1.73–1.44 (m, 15H), 1.21–1.08 (m, 2H), 1.16 (d, J = 6.9 Hz, 3H, H-21), 0.90–0.87 (m, 1H), 0.86 (s, 3H, H-19), 0.77 (s, 3H, H-18), 0.71 (d, J = 4.9 Hz, 3H, H-27), 0.67–0.61 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.7 (C-22), 103.1 (C-1″), 102.4 (C-1′), 81.5 (C-16), 78.9 (C-4′), 78.2 (C-6), 77.5 (C-5′), 77.2 (C-3′), 75.9 (C-2′), 74.4 (C-4″), 73.2 (C-3″), 73.1 (C-2″), 70.8 (C-5″), 68.9 (C-3), 67.3 (C-26), 63.5, 62.0 (C-6′), 56.8, 54.6, 52.6, 43.1, 42.5, 41.3, 40.5, 38.1, 37.0, 34.7, 32.6, 32.3, 31.1, 30.4, 29.9, 29.7, 21.8, 19.0 (C-6″), 17.8 (C-27), 17.1 (C-19), 15.5 (C-21), 14.0 (C-18); HRMS (ESI) calcd for $C_{39}H_{64}O_{13}Na$ [M+Na]$^+$: 763.4239, found: 763.4281.

4.3.58. Chlorogenin 3β-*O*-{4-*O*-[4-*O*-(α-L-rhamnopyranosyl)-α-L-rhamnopyranosyl]-β-D-glucopyranoside} (73)

By the similar procedure for the synthesis of **63**, treatment of compound **49** (88 mg, 0.054 mmol) afforded **73** (19.5 mg, 0.022 mmol, 41%) as a white solid: mp 238 °C; $[\alpha]_D^{25}$ −41.7 (c 0.05, MeOH); ^{1}H NMR (pyridine-d_5, 600 MHz) δ 6.38 (s, 1H, H-1‴), 6.38 (s, 1H, H-1″), 4.99 (d, J = 7.5 Hz, 1H, H-1′), 4.95–4.88 (m, 1H, H-5″), 4.88 (s, 1H, H-2‴), 4.73–4.68 (m, 1H, H-3″), 4.62 (s, 1H, H-2″), 4.58–4.54 (m, 2H, H-3‴, H-16), 4.52–4.48 (m, 3H, H-6a′, H-5‴, H-4″), 4.45–4.41 (m, 1H, H-4′), 4.36–4.32 (m, 1H, H-6b′), 4.30–4.28 (m, 1H, H-4‴), 4.26 (d, J = 7.9 Hz, 1H, H-2′), 4.22–4.12 (m, 2H, H-3′), 4.06–4.02 (m, 1H, H-6), 3.78–3.76 (m, 1H, H-5′), 3.73–3.69 (m, 1H, H-3), 3.63–3.58 (m, 1H, H-26α), 3.41 (t, J = 10.4 Hz, H-26β), 2.12–1.98 (m, 6H), 1.74–1.51 (m, 6H), 1.48–1.18 (m, 12H), 1.65 (d, J = 6.3 Hz, 3H, H-6‴), 1.18 (d, J = 6.8 Hz, 3H, H-21), 1.11 (s, 3H, H-19), 0.89–0.85 (m, 1H), 0.82 (s, 3H, H-18), 0.73 (d, J = 5.4 Hz, 3H, H-27), 0.65–0.51 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.3 (C-22), 103.1 (C-1‴), 100.9 (C-1″), 99.8 (C-1′), 80.5 (C-16), 80.4 (C-4″), 79.6 (C-3′), 79.3 (C-4′), 78.9 (C-5′), 77.4 (C-2′), 74.6 (C-6), 74.0 (C-4‴), 73.2 (C-3″), 73.9 (C-2″), 73.0 (C-3‴), 72.2 (C-2‴), 68.9 (C-5‴), 68.1 (C-3), 67.3 (C-5″), 65.9 (C-26), 64.4 (C-6′), 63.1, 56.9, 54.7, 52.6, 43.2, 42.1, 41.6, 38.7, 37.4, 34.7, 32.8, 32.5, 34.7, 32.6, 31.0, 30.4, 30.2, 21.7, 19.5 (C-6″), 19.3 (C-6‴), 17.9 (C-27), 17.5 (C-18), 15.4 (C-21), 14.3 (C-19); HRMS (ESI) calcd for $C_{45}H_{74}O_{17}Na$ [M+Na]$^+$: 909.4818, found: 909.4799.

4.3.59. Chlorogenin 3β-*O*-{2-*O*-(α-L-rhamnopyranosyl)-4-*O*-[4-*O*-(α-L-rhamnopyranosyl)-α-L-rhamnopyranosyl]-β-D-glucopyranoside} (74)

By the similar procedure of synthesis of **63**, treatment of **52** (83 mg, 0.04 mmol) with acetic acid, followed by LiOH hydrolysis and hydrogenation afforded **74** (14 mg, 31%) as a white solid: mp 220 °C; $[\alpha]_D^{25}$ −89.9 (c 0.05, MeOH); ^{1}H NMR (pyridine-d_5, 600 MHz) δ 6.38 (s, 1H, H-1‴), 6.30 (s, 1H, H-1⁗), 5.84 (s, 1H, H-1″), 5.06–5.01 (m, 1H, H-5‴), 5.00 (d, J = 7.8 Hz, 1H, H-1′), 4.95–4.91 (m, 1H, H-5″), 4.91 (d, J = 0.7 Hz, 1H, H-2⁗), 4.81 (d, J = 1.6 Hz, 1H, H-2‴), 4.62 (dd, J = 3.1, 9.2 Hz, 1H, H-3‴), 4.57–4.52 (m, 3H, H-3″, H-16, H-2″), 4.52 (dd, J = 3.2, 9.2 Hz, 1H, H-3⁗), 4.46 (t, J = 9.2 Hz, 1H, H-4″), 4.43–4.30 (m, 4H, H-4′, H-5⁗, H-4‴, H-4⁗), 4.20–4.07 (m, 3H, H-2′, H-6a′, H-3′), 4.04 (dd, J = 3.3, 11.9 Hz, 2H, H-6b′, H-6), 3.61–3.52 (m, 2H, H-3, H-26α), 3.50–3.45 (m, 2H, H-5′, H-26β), 2.22–1.81 (m, 5H), 1.79 (d, J = 6.1 Hz, 3H, H-6‴), 1.77–1.64 (m, 8H), 1.63 (d, J = 6.5 Hz, 3H, H-6⁗), 1.60 (d, J = 6.3 Hz, 3H, H-6″), 1.48–1.42 (m, 2H), 1.34–1.17 (m, 4H), 1.16 (d, J = 6.9 Hz, 3H, H-21), 1.1–0.95 (m, 1H), 0.96 (s, 3H, H-19), 0.91–0.89 (m, 1H), 0.85 (s, 3H, H-18), 0.71 (d, J = 5.4 Hz, 3H, H-27), 0.67–0.65 (m, 1H); ^{13}C NMR (pyridine-d_5, 150 MHz) δ 109.6 (C-22), 103.7 (C-1⁗), 102.7 (C-1‴), 102.6 (C-1″), 99.9 (C-1′), 81.5 (C-16), 80.8 (C-4″), 78.6 (C-2′), 78.2 (C-3′), 78.1 (C-4′), 77.5 (C-6), 77.3 (C-5′), 74.6 (C-4‴), 74.5 (C-4⁗), 73.7 (C-3″), 73.4 (C-2″), 73.3 (C-3⁗), 73.2 (C-3‴), 73.1 (C-2⁗), 72.9 (C-2‴), 70.8 (C-5⁗), 69.9 (C-5‴), 68.9 (C-3), 68.7 (C-5″), 67.3 (C-26), 63.4, 61.7 (C-6′), 56.8, 54.5, 52.6, 43.1, 42.4, 41.2, 40.5, 38.1, 37.1, 34.7, 32.6, 32.2, 31.0, 30.2, 29.7, 29.3, 21.7, 19.3 (C-6″), 19.1 (C-6‴), 18.9 (C-6⁗), 17.7 (C-27), 17.0 (C-18), 15.4 (C-21), 14.0 (C-19); HRMS (ESI) calcd for $C_{51}H_{84}O_{21}Na$ [M+Na]$^+$: 1055.5397, found: 1055.5359.

Acknowledgements

We gratefully acknowledge the National Science Council of Taiwan ROC (NSC 98–2320-B-002-017-MY3) and Academia Sinica for financial support. We thank Professor Y. S. Edmond Cheng at the Genomics Research Center of Academia Sinica for the influenza virus assay.

Supplementary data

Supplementary data (1D and 2D NMR spectra for compounds) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carres.2013.04.022.

References

1. Zhang, J.-B.; Hui, Y.-Z. *Chin. J. Org. Chem.* **2000**, *20*, 663–688.
2. Chiang, H. C.; Tseng, T. H.; Wang, C. J.; Chen, C. F.; Kan, W. S. *Anticancer Res.* **1991**, *11*, 1911–1917.
3. Wang, Z.; Zhou, J. B.; Ju, Y.; Zhang, H.; Liu, M.; Li, X. *Biol. Pharm. Bull.* **2001**, *24*, 159–162.
4. Cai, J.; Liu, M.; Wang, Z.; Ju, Y. *Biol. Pharm. Bull.* **2002**, *25*, 193–196.
5. Li, M.; Han, X.; Yu, B. *Carbohydr. Res.* **2003**, *338*, 117–121.
6. Wang, Y.; Zhang, Y.; Zhu, Z.; Zhu, S.; Li, Y.; Li, M.; Yu, B. *Bioorg. Med. Chem.* **2007**, *15*, 2528–2532.
7. Kubo, S.; Mimaki, Y.; Terao, M.; Sashida, Y.; Nikaido, T.; Ohmoto, T. *Phytochemistry* **1992**, *31*, 3969–3973.
8. Song, G. P.; Yang, S.; Zhang, W.; Cao, Y. L.; Wang, P.; Ding, N.; Zhang, Z. H.; Guo, Y.; Li, Y. X. *J. Med. Chem.* **2009**, *52*, 7368–7371.
9. Ding, N.; Chen, Q.; Zhang, W.; Ren, S.; Guo, Y.; Li, Y. *Eur. J. Med. Chem.* **2012**, *53*, 316–326.
10. Schlunzen, F.; Zarivach, R.; Harms, J.; Bashan, A.; Tocilj, A.; Albrecht, R.; Yonath, A.; Franceschi, F. *Nature* **2001**, *413*, 814–821.
11. Hansen, J. L.; Ippolito, J. A.; Ban, N.; Nissen, P.; Moore, P. B.; Steitz, T. A. *Mol. Cell* **2002**, *10*, 117–128.
12. Ikeda, T.; Miyashita, H.; Kajimoto, T.; Nohara, T. *Tetrahedron Lett.* **2001**, *42*, 2353–2356.
13. Miyashita, H.; Kai, Y.; Noharab, T.; Ikeda, T. *Carbohydr. Res.* **2008**, *343*, 1309–1315.
14. Randolph, J. T.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1995**, *117*, 5693–5700.
15. Verma, P.; Kabra, V. K.; Mukhapadhyay, B. *Carbohydr. Res.* **2011**, *346*, 2342–2347.
16. Deng, S.; Yu, B.; Hui, Y. *Tetrahedron Lett.* **1998**, *39*, 6511–6514.
17. Li, C.; Yu, B.; Liu, M.; Hui, Y. *Carbohydr. Res.* **1998**, *306*, 189–195.
18. Jiang, L.; Chan, T. H. *J. Org. Chem.* **1998**, *63*, 6035–6038.
19. Li, B.; Yu, B.; Hui, Y.; Li, M.; Han, X.; Fung, K. P. *Carbohydr. Res.* **2001**, *331*, 1–7.
20. Yu, B.; Tao, H. *Tetrahedron Lett.* **2001**, *42*, 2405–2407.
21. Yu, B.; Tao, H. *J. Org. Chem.* **2002**, *67*, 9099–9102.
22. Du, Y.; Gu, G.; Wei, G.; Hua, Y.; Linhardt, R. J. *Org. Lett.* **2003**, *5*, 3627–3630.
23. Zhang, Y.; Li, Y.; Guo, T.; Guan, H.; Shi, J.; Yu, Q.; Yu, B. *Carbohydr. Res.* **2005**, *340*, 1453–1459.
24. Yu, B.; Sun, J. *Chem. Asian J.* **2009**, *4*, 642–654.
25. Wong, C.-H.; Ye, X.-S.; Zhang, Z. *J. Am. Chem. Soc.* **1998**, *120*, 7137–7138.
26. Wunberg, T.; Kallus, C.; Opatz, T.; Henke, S.; Schmidt, W.; Kunz, H. *Angew. Chem.* **1998**, *110*, 2620–2622. *Angew. Chem. Int. Ed.* **1998**, *37*, 2503–2505.
27. Daragics, K.; Fugedi, P. T. *Org. Lett.* **2010**, *12*, 2076–2079.
28. David, S.; Malleron, A.; Dini, C. *Carbohydr. Res.* **1989**, *188*, 193–200.
29. DeNinno, M. P.; Etienne, J. B.; Duplantier, K. C. *Tetrahedron Lett.* **1995**, *36*(5), 669–672.
30. Munday, S. C.; Wilkins, A. L.; Miles, C. O.; Holland, P. T. *J. Agric. Food Chem.* **1993**, *41*, 267–271.
31. Gerlier, D.; Thomasset, N. *J. Immunol. Methods* **1986**, *94*, 57–63.